PB82-208273

Analytical Methods for Hazardous Organics in Liquid Wastes from Coal Gasification and Liquefaction Processes

University of Southern California
Los Angeles

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-208273

EPA-600/4-82-038
April 1982

ANALYTICAL METHODS FOR HAZARDOUS ORGANICS IN LIQUID WASTES FROM COAL GASIFICATION AND LIQUEFACTION PROCESSES

by

T.F. Yen
J.I.S. Tang
Martha Washburne
Shoreh Cohanim

School of Engineering
University of Southern California
Los Angeles, California 90007

Contract No. R806167-01-0
Project Officer
F. K. Kawahara
Environmental Monitoring & Support Laboratory
Environmental Protection Agency
Cincinnati, Ohio 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

Environmental Monitoring & Support Laboratory
Environmental Protection Agency
Cincinnati, Ohio 45268

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-038	ORD Report	PB82 208273

4. TITLE AND SUBTITLE
Analytical Methods for Hazardous Organics in Liquid Wastes from Coal Gasification and Liquefaction Processes

5. REPORT DATE
April 1982

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
T. F. Yen, J.I.S. Tang, Martha Washburne
Shoreh Cohanim, F. K. Kawahara

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of Southern California
Los Angeles, CA 90007

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
R806167-01-1

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Project Report 2/79 To 10/80

14. SPONSORING AGENCY CODE
EPA 600/06

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This study was conducted by the University of Southern California group to provide methods for the analysis of coal liquefaction wastes from coal conversion processing plants. Several methods of preliminary fractionation prior to analysis were considered. The most satisfactory method is that employing column separation, using macroreticular absorbent resins and dividing the wastewaters into hydrophobic and hydrophilic fractions. By subsequent use of ion exchange resins, each fraction was subdivided into acid, neutral, and basic subfractions. These subfractions yielded materials suitable for gas chromatography/mass spectrometric analysis performed by Finnigan Company. To identify the numerous compounds contained in each subfraction produced by the resin chromatographic separation, a GC/MS equipped with a computer library of mass spectra of 31,331 compounds was used. The peaks eluting from the GC can be individually and immediately analyzed for their spectra which can be compared to those in the computer library.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to public	Unclassified	96
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

DISCLAIMER

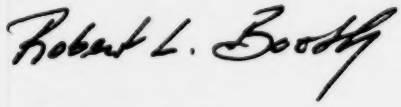
This report has been reviewed by the Environmental Monitoring and Support Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This research reports on an analysis of coal process wastewaters to study the organic pollutants in it. The potential for mutagenicity of coal liquid water extracts as measured by the Ames test were also investigated.



Robert L. Booth
Acting Director
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio

ABSTRACT

This report describes the progress made in developing a systematic analytical protocol for identifying and quantifying predominant hazardous organic chemicals present in the wastewaters of coal gasification and liquefaction plants. The first phase consisted of development of a qualitative scheme including chromatographic separation, total organic carbon determination, infrared spectrometry (IR), gas chromatography and mass spectrometry (GC-MS). An additional task of testing coal liquids, the raw end products of coal liquefaction, for mutagenicity was carried out. Minimal mutagenicity was found in three out of four water extracts taken from coal liquids.

The second phase consisted of the quantitation of the compounds detected in the wastewaters. Twenty hazardous organic chemicals named in the EPA priority list were detected in varying quantities in the wastewaters. Polynuclear aromatic hydrocarbons (PAH) were found to be present in concentrations yielding gram quantities in daily operation of an average pilot plant. Nitrogenous compounds were present at the same level, and one particular, N-nitrosodimethylamine, was present at kilogram levels daily. Phenol was present in concentrations high enough to be potentially recoverable economically. Phenolic compounds were the most predominant organic species found.

Method development incorporated the use of macroreticular resins for the initial separation of the organics in the wastewaters, sensitive GC-MS and IR identification and quantitative computer matching of mass spectra. A protocol of methods will be assembled into handbook form for the third phase of this study. Further analysis of coal wastewaters for organometallics, metals and heteroatomic organics will also be carried out in this phase.

This report was submitted in partial fulfillment of Contract No. R806167-01-1 by the University of Southern California under the sponsorship of the U.S. Environmental Protection Agency. The report covers the periods from February 1979 to October 1980.

CONTENTS

Foreword iii
Abstract iv
Figures vii
Tables viii
Abbreviations and Symbols xi
Acknowledgments xiii
SECTION 1. INTRODUCTION 1
SECTION 2. CONCLUSIONS 5
SECTION 3. RECOMMENDATIONS 6
SECTION 4. DISCUSSION OF THE METHODS 7
Column Separation 7
Identification Analysis 10
SECTION 5. EXPERIMENTAL METHODS 11
Preliminary Sample Treatment 11
Sample Acquisition and Storage 11
Analytical Procedure 11
Physical and Chemical Properties Analysis 11
Organic Analysis 14
Column Adsorption Separation 14
Total Organic Carbon Analysis for Separated Fractions . 14
Infrared Spectrometry Study of Separated Fraction . . . 16
Preliminary Mass Spectrometry Study 16
Gas Chromatograph-Mass Spectrometry Analysis 16
Computer Analysis of GC-MS Data to Identify Organic Compounds 23
Quantitative Analysis of Priority Pollutants. 23
Mutagenic Potential Assessment of Coal Liquids. 23
Origin 23
Mutagenicity Test for Coal Liquid Water Extract 25

CONTENTS (Continued)

SECTION 6. RESULTS AND DISCUSSION 31
General Statement 31
Polynuclear Aromatic Hydrocarbons (PAH). 43
Phenols 43
Nitrogen Compounds 43
Chlorinated Hydrocarbons 48
Mutagenicity Analysis of Coal Liquid Water Extracts. 48
Summary 51
REFERENCES 53
APPENDICES 54
A. Protocol of GC-MS Identification Procedure 54
B. Priority Pollutant List 82

FIGURES

Number		Page
1	Hypothetical Structure of Coal	2
2	Compounds Identified in Solvent Coal Process	3
3	Structure of Amberlite Resin	9
4	Schematic Diagrams of Analytic Procedure	12
5	Flow Diagram of Analytic Procedure	15
6	IR Spectrum of HO Neutral No. 1 Sample	18
7	IR Spectrum of HO Neutral No. 2 Sample	19
8	Mass Spectrum of HO Neutral Sample No. 1	21
9	Mass Spectrum of HO Neutral Sample No. 2	22
10	Typical Nitrogen Structure of Coal	46
11	Compounds Identified as Indigenous to Coal	47
12	Summary of the Concentration of Identified Pollutants.	52
13	Reconstructed Ion Chromatogram For Water Sample No. 1, Hydrophobic Neutral Fraction	55
14	Reconstructed Ion Chromatogram For Water Sample No. 1, Hydrophobic Neutral Fraction	56

TABLES

Number		Page
1	Typical Properties of Amberlite Polymeric Adsorbents	8
2	Analysis of Chemical Properties in Two Coal Waste Water Samples.	13
3	Percentage of Total Organic Carbon Distribution in Separated Fractions	17
4	IR Absorption of Organic Compounds in Coal Waste Water	20
5	GC-MS Operating Parameters	24
6	Identification of Major Compounds in a Coal-Derived Fluid.	26
7	Properties of Coal Liquids Used.	29
8	Weight Percentage of Water Soluble Organics from Coal Liquid Samples.	30
9	Compounds Identified from HO Neutral Fraction in No. 1 Water Smaple	32
10	Compounds Identified from HO Base Fraction in No. 1 Water Sample	33
11	Compounds Identified from HO Acid Fraction in No. 1 Water Sample	33
12	Compounds Identified from HI Neutral Fraction in No. 1 Water Sample	34
13	Compounds Identified from HI Base Fraction in No. 1 Water Sample	34
14	Compounds Identified from HI Acid Fraction in No. 1 Water Sample	35
15	Compounds Identified from HO Neutral Fraction in No. 2 Water Sample	36
16	Compounds Identified from HO Base Fraction in No. 2 Water Sample	37
17	Compounds Identified from HO Acid Fraction in No. 2 Water Sample	38

TABLES (continued)

Number		Page
18	Compounds Identified from HI Neutral Fraction in No. 2 Water Sample	38
19	Compounds Identified from HI Base Fraction in No. 2 Water Sample	39
20	Compounds Identified from HI Acid Fraction in No. 2 Water Sample	39
21	Quantitative Analysis of HO Neutral Fraction in No. 1 Sample	40
22	Quantitative Analysis of HI Base Fraction in No. 2 Sample.	41
23	Quantitative Analysis of HO Base Fraction in No. 2 Sample.	42
24	Quantitative Analysis of HI Acid Fraction in No. 1 Sample.	42
25	Quantities of PAHs in a Coal-Derived Liquefaction Product.	44
26	Estimated Quantities of PAHs in Coal Process Waste Water	45
27	Qualitative Test for Mutagenicity of Coal Liquid Water Extract Sample	49
28	Mutagenicity Test for Coal Liquid Water Extracts	50
29	Peak #77 M/E 91	57
30	Peak #131 M/E 43	58
31	Peak #193 M/E 108	59
32	Peak #244 M/E 94	60
33	Peak #264 M/E 107	61
34	Peak #303 M/E 107	62
35	Peak #315 M/E 107	63
36	Peak #324 M/E 107	64
37	Peak #331 M/E 121	65

TABLES (continued)

Number		Page
38	Peak #335 M/E 121	66
39	Peak #343 M/E 121	67
40	Peak #352 M/E 121	68
41	Peak #382 M/E 133	69
42	Peak #394 M/E 133	70
43	Peak #451 M/E 144	71
44	Peak #506 M/E 170	72
45	Peak #614 M/E 107	73
46	Peak #684 M/E 149	74
47	GC-MS Computer Match Summary for Hydrophobic Neutral Fraction of Water Sample No. 1	75
48	GC-MS Computer Match Summary HO Basic Water Sample No. 1	76
49	GC-MS Computer Match Summary HO Acidic Water Sample No. 1	76
50	HI Neutral Water Sample No. 1	77
51	HI Acidic Water Sample No. 1	77
52	HI Acidic Water Sample No. 2	78
53	HO Neutral Water Sample No. 2	78
54	HO Basic Water Sample NO. 2	79
55	HO Acidic Water Sample No. 2	79
56	HO Acidic Water Sample No. 2	80
57	HO Acidic Water Sample No. 2	80
58	HO Acidic Water Sample No. 2	81

LIST OF ABBREVIATIONS

ABBREVIATIONS

BOD_5	--biological oxygen demand (5 days)
COD	--chemical oxygen demand
DMSO	--dimethyl sulfoxide
GC	--gas chromatography
GC-MS	--gas chromatography and mass spectrometry
gm	--gram
HI	--hydrophilic
HO	--hydrophobic
IR	--infrared spectrometry
kg	--kilogram
Lc	--liquid chromatography
Lc-MS	--liquid chromatography and mass spectrometry
M/E	--mass/electron
µg	--microgram
M.W.	--molecular weight
N/C	--negative control
PAH	--polynuclear aromatic hydrocarbon
pg	--picogram
ppb	--parts per billion
ppm	--parts per million
psi	--pounds per square inch

LIST OF ABBREVIATIONS (continued)

ABBREVIATIONS

RIC	--reconstructed ion chromatography
TOC	--total organic carbon
wt	--weight

ACKNOWLEDGMENTS

The authors gratefully acknowledge the guidance and counsel of Dr. Fred K. Kawahara, Project Officer, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. The authors also express their appreciation to R. E. Perrussel of Pittsburg & Midway Coal Mining Co., DuPont, Washington and J. A. Klein of Oak Ridge Division of Union Carbide Co., Oak Ridge, Tennessee for the samples of coal process wastewaters.

Special acknowledgment is made of the technical contributions of Drs. Paul Taylor and Rong Hwang.

SECTION 1

INTRODUCTION

Gasification and liquefaction of coal will generate hundreds of organic species which could contaminate the water associated with the conversion processes, and pose a possible threat to the environment.

A majority of coal plant waste streams released into the environment are wastewaters from coal conversion process steps (Oak Ridge National Laboratory, 1977)[1]. This includes wastewater originating as moisture in the coal, water of constitution or decomposition, water added for stoichiometric process requirements, and water introduced by product recovery or gas scrubbing. These types of wastewater contain soluble and suspended organics and are produced in both the coal gasification and liquefaction processes. These wastewaters are formed under the following conditions:

1. When gases are scrubbed to remove soluble contaminants, quenched to control operating temperature, compressed, or dehydrated;
2. When steam used in the unit process cools and condenses or is reformed during methanation or hydrotreating;
3. When the product oil is formed by hydrogenation or pyrolysis and is allowed to settle for product recovery; or
4. When slags and ash are water-quenched for slurry removal.

The contaminant content of wastewater varies according to feed coal ranks, conversion process types and severity, and upstream subsidiary treatments. This wastewater is usually also heavily laden with inorganic cations and anions which may consequently form double salts, complexes. Additionally, the specific relationship of the inorganics to the dissolved organic species further complicates the problems of treatment and abatement.

The chemical species are varied and numerous because they represent practically all the organic compounds found in coal (Rubin and McMichael, 1975)[2]. The structure of coal, as recently proposed (Figure 1) (Victor, 1977)[3] can be visualized as consisting of islands of aromatic and heterocyclic clusters connected by weak linkages, such as hydrogen bonding, quaternization, or donor-acceptor complexation (Yen, 1976)[4]. The coal conversion processes involve a variety of reactions with pressure, heat, catalysts, and/or water. These reactions produce many classes of organic species. Some of the typical compounds identified (Peterson, 1975)[5] are presented in Figure 2. PAH, phenolics, nitrogenous compounds, other oxygen-functional compounds, and organometallics fall under the classification of potentially hazardous materials (EPA, 1975)[6].

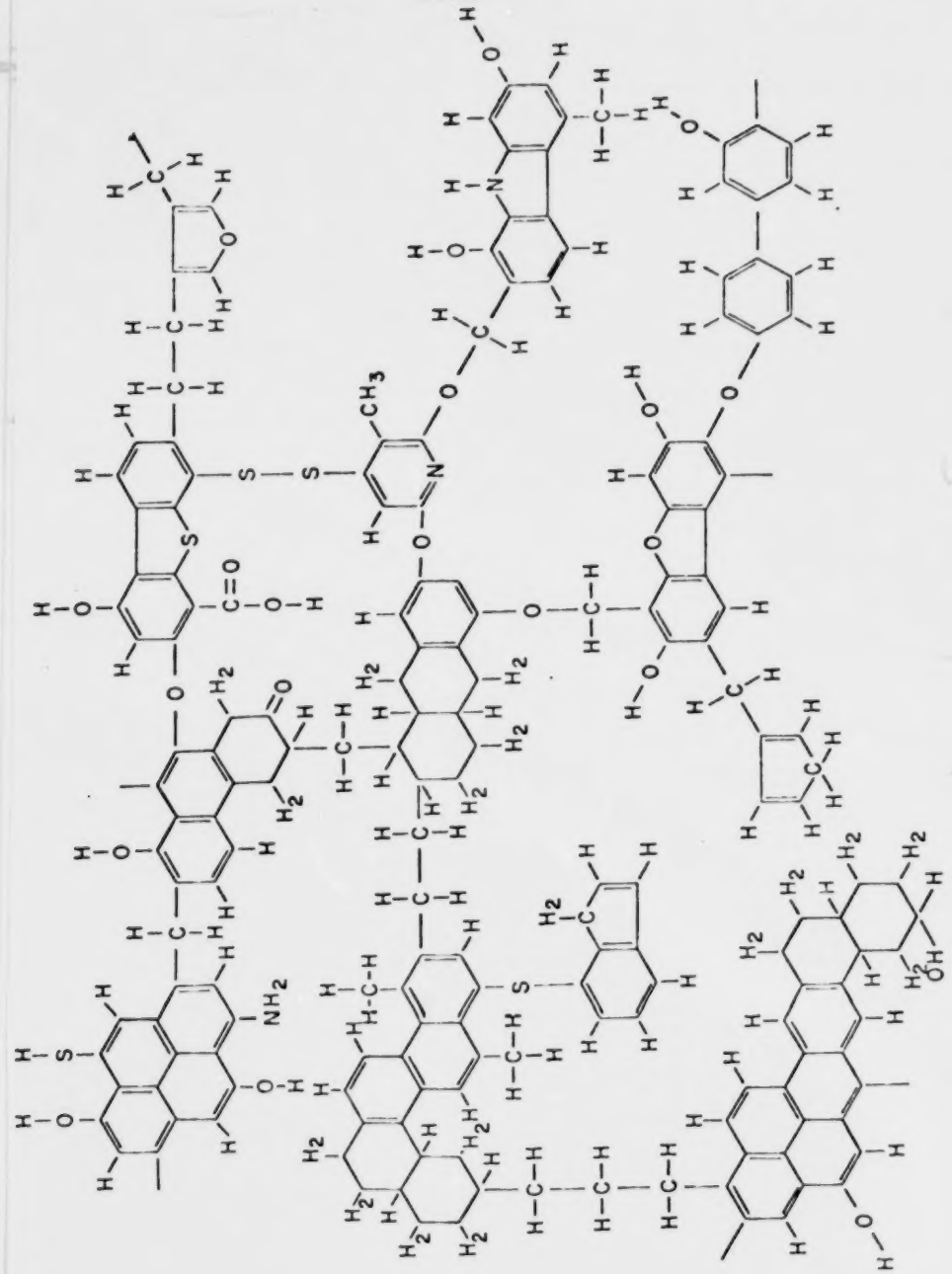


Figure 1. Hypothetical Structure of Coal. (Refs. 3,4 and 11)

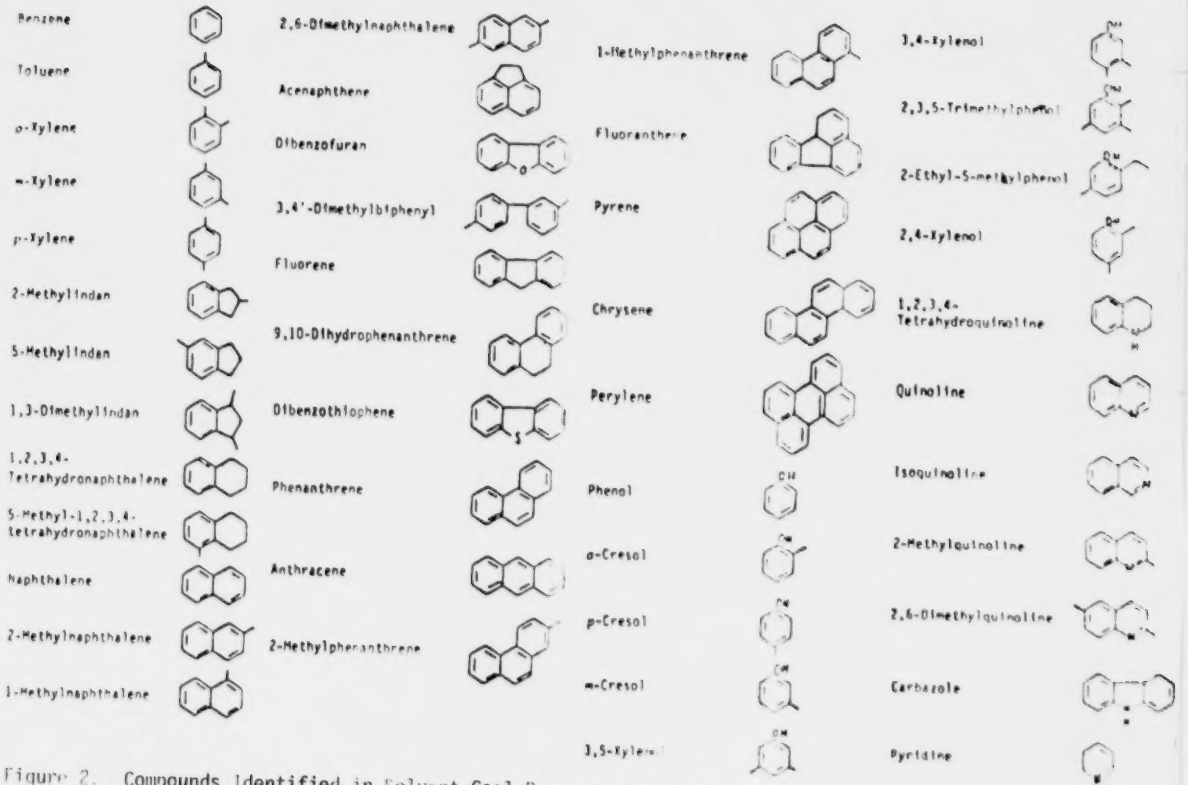


Figure 2. Compounds Identified in Solvent Coal Process. (Ref. 5)

The overall objective of this project was to develop an analytical method enabling identification and analysis of hazardous organic compounds in wastewater effluents from coal conversion processes. A systematic scheme of isolating hazardous compounds as well as study of their nature and properties would help in designing a treatment method later. Development of a complete protocol for major hazardous compounds will lead to monitoring and controlling them so that potential hazards to human health and the general environment may be minimized.

The research work consisted of three phases:

1. Development of a systematic scheme of separation and identification for the following four types of hazardous compounds:

   a. PAH

   b. phenolics

   c. nitrogenous compounds

   d. other oxygen functional compounds

2. Quantification of the identified species in various coal waste effluents.

3. Development of a complete protocol in handbook form for all hazardous compounds mentioned in Phase One and also including:

   e. organometallics

   f. metals

   g. other species identified in this study and known to be hazardous

This report pertains to Phase One and part of Phase Two.

SECTION 2

CONCLUSIONS

Using the procedures developed in this laboratory, several potentially hazardous compounds listed by the EPA as "Priority Pollutants" (EPA-650/2-75-030) were found in coal conversion process wastewaters. In certain cases concentrations are high enough to have a potentially significant environmental impact.

Twenty compounds which make up 15 per cent of the priority pollutants on the list, were quantitatively found to be present at nanogram levels or higher. Compounds in highest quantity were phenolics, with significant levels of two other compounds, n-nitroso-dimethylamine and di-n-butylphthalate. Most of the PAH known to be in coal liquids were also found in the wastewater. Chlorinated aromatics were detected qualitatively, and quantitative methods for these compounds are under investigation.

The daily quantities of dominant species produced depend on the amount of liquid effluents produced from the conversion plant in question. The amount of liquid effluents from an average size coal process plant with wastewater production levels of 3,785 liter/min (1,000 gal/min) is used here to estimate the quantity of pollutants on a daily basis.

Phenol may be present in economically attractive quantities for recovery. In a liquefaction plant 1.5×10^4 kg and in a gasification plant 3.5×10^4 kg of phenol are produced daily. Other species in significant concentration include PAH, which are produced in gram quantities daily by an average plant, and nitrogenous compounds which are produced in gram and kilogram quantities daily.

Bulk extracts of coal liquids were found to be mutagenic in three out of the four samples tested. An accidental spill of coal liquids could represent danger to groundwater supplies, especially since the water soluble components of coal liquids are the ones most likely to be mutagenic.

The presence of hazardous compounds in coal liquids and in coal conversion wastewaters indicates the need for a routinized protocol of identification and quantitation for the monitoring of plant effluents. Such a protocol, in handbook format, will be presented in the final report.

SECTION 3

RECOMMENDATIONS

The current procedures are limited with respect to the range of molecular weights of the organic compounds in waste effluents. GC-MS cannot effectively detect species with molecular weights greater than 500. It is recommended that an interface of a high performance liquid chromatograph with a mass spectrometer, known as LC-MS be used. This will increase the range of molecular weights to 1000 or beyond. Accurate assessment of environmental impact requires that these larger compounds not be neglected in this study. Organometallics of low volatility will also be detectable.

There are a number of advantages to LC separation. Separations may be based on polarity and/or molecular size. In polarity separations, columns including Corasil, Micro-Porasil, normal phase Micro-Bondapack-NH_2, reverse phase Micro-Bondapak-C_{18}, and aqueous compatible size exclusion columns can be used. In molecular size separation, Micro-Styrogel columns can be considered for use.

Another improvement in the analysis of multicomponent systems is the use of extremely long (greater than 100 meters) lengths of capillary glass columns. Resolution of mixtures into individual compounds is greatly improved, making accurate identification of constituents by mass spectroscopy more likely. An extension of sensitivity of the lower end of the quantity range occurs, thereby reducing the relative error in quantitation and improving precision. Determination of extremely small concentrations is justified since extremely large quantities of wastewater produced daily may accumulate small concentrations of toxic substances to a hazardous daily output.

These recommendations should be considered in the analysis of wastewaters of coal gasification and liquefaction plants as this fractionation method has provided for separated fractions totaling 80.3 and 92.5% of the original for the two different samples as shown in Table 3, page 17. In addition to these attractive values, this procedure has yielded separated fractions that may be analyzed suitably by GC/MS. This is indicated by the many compounds identified in the preliminary survey. In the hydrophobic fractions of sample No. 1, 19, and 6 compounds were found in the neutral, basic, and acidic fractions (Tables 47 thru 49), respectively. In the hydrophilic fractions, 4, 6, and 11 compounds were identified in the neutral, basic, and acidic fractions (Tables 50 thru 52), respectively. These are the numbers taken for the computer-library matched compounds. Other compounds were identified with less confidence in their quantitative assessment.

SECTION 4

DISCUSSION OF METHODS

The analytical procedure developed for this study combined the use of physicochemical separations and sophisticated spectrometric methods necessary in the resolution and characterization of complex organic matter.

COLUMN SEPARATION

A three dimensional co-polymer resin possessing macroreticular or macroporous structure is considered to be the most effective means of preliminary separation of organics in aqueous samples. These porous polymeric resins will function as the sorbing agent for organics. The full line of macroreticular adsorbent resins includes a spectrum of surfaces from the least polar to the most polar for adsorbing compounds with different polarities. The chemical structures and physical properties of these resins are shown in Figure 3 and Table 1, respectively (Amberlite Polymeric Adsorption, Rohm and Haas Company, 1978)[7].

The pre-separation of organics in coal wastewater via these resins is done for the following reasons:

1. The resin has a homogeneous surface, permitting the operation of only one adsorption mechanism at a time. Hence, solutes can be quantitatively adsorbed or desorbed.

2. The large surfaces area produces high exchange capacity as well as good chemical and structural stability.

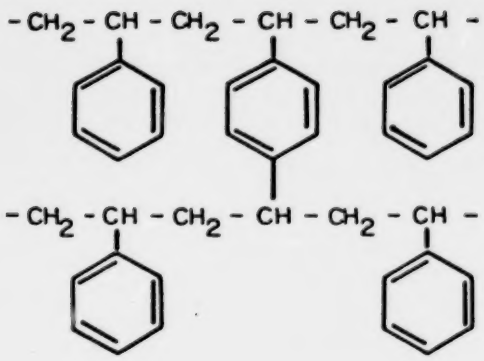
3. No high energy process, such as heat, is used which might alter the nature of the organic solutes or evaporate the volatile compounds which have relatively low boiling points.

The polymer resin used in this study is able to fractionate organic solute mixtures into more homogeneous fractions based on sorption mechanisms without serious alteration of the solutes or solute matrix. The general theory that hydrophobic (HO) or nonpolar molecules are attracted to hydrophobic surfaces, and hydrophilic (HI) or polar molecules to hydrophilic or polar surfaces, is adopted in this scheme. Thus, adsorbents of intermediate polarity such as Amberlite XAD-7 and XAD-8 have an attraction for molecules of completely hydrophobic nature, or essentially hydrophobic compounds with some polar functionality.

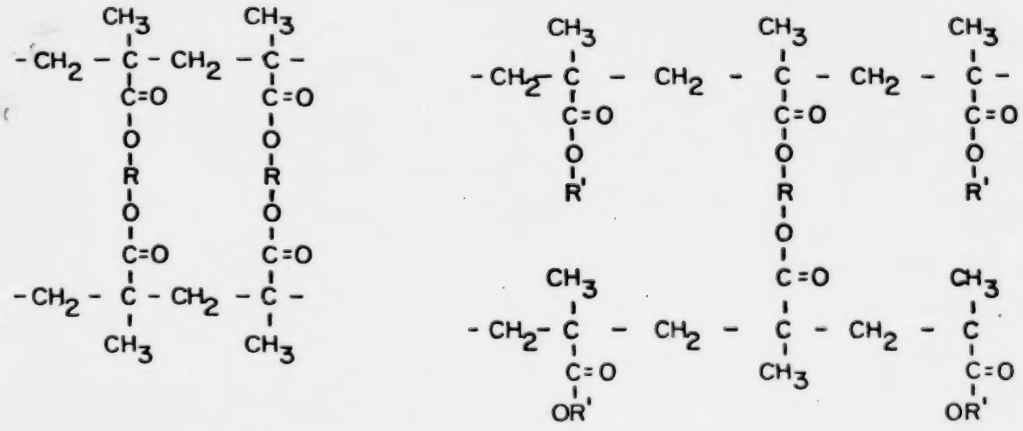
To adsorb hydrophilic compounds of polar or neutral functionalities, ion

TABLE 1. TYPICAL PROPERTIES OF AMBERLITE POLYMERIC ADSORBENTS (Ref. 7)

Chemical Nature	Porosity Volume %	True Wet Density (grams/cc)	Surface Area (m^2/gram)	Average Pore Dia. (Angstroms)	Skeletal Density (grams/cc)	Nominal Mesh Sizes
			Nonpolar			
XAD-1 Polystyrene	37	1.02	100	100	1.07	20 to 60
XAD-2 Polystyrene	42	1.02	300	90	1.07	20 to 60
XAD-4 Polystyrene	45	1.02	725	40	1.08	20 to 60
			Intermediate Polarity			
XAD-7 Acrylic Ester	55	1.05	450	90	1.24	20 to 60
XAD-8 Acrylic Ester	52	1.09	160	225	1.23	25 to 60



(a)



(b)

Figure 3. Structure of Amberlite Resin
(a) XAD-2, XAD-4 (b) XAD-7, XAD-8

exchange resins were used.

The complex mixture of organic solutes in the wastewater was fractionated into different compound classes. The first classification step was to separate the organics into HO and HI compounds. Further classification was based on organic acid base characteristics. The details of the column separation procedures are reported in Section 5.

IDENTIFICATION ANALYSIS

Chemical characterization of fractionated organics is determined via total organic carbon (TOC) analysis, infrared spectrometry, and mass spectrometry. These methods describe organic carbon distribution, functional groups, and mass range, respectively. Identification of organic compounds in different fractions was achieved by GC-MS. Combination of GC-MS and computer analysis is an extremely useful technique for identification and analysis of trace organic compounds. Since it provides relatively pure mass spectra for a large number of individual components in fairly complex mixtures.

The organic species in different fractions are extracted with solvent and concentrated for injection into the GC. Each extract passes into the ion volume of the mass spectrometer, which automatically scans the mass range if there is a GC signal present. The filtered ions pass through the ion detector according to their molecular weights. The ion current in then amplified and plotted against the spectrum scan time base. The computer stores the output and plots a reconstructed ion chromatogram (RIC) of total ion amplitude versus the spectrum number. Identification is accomplished by plotting the mass spectrum of a specified peak or by comparing the spectrum with data stored in the reference library for a specific mass/electron (m/e) value. The quantitative analysis is determined by GC with a flame ionization detector and a data processor for measuring relative retention time and calculating response factors compared with internal standards.

The Finnigan 4000 Series GC-MS system with Incos 2000 Mass Spectrometer Data System can measure samples as small as 50 picogram (pg) in selected ion monitoring modes, with 100 pg full spectrum sensitivity, employing optimum operating conditions for measurement. Mass range covers from 2 to 2000 atomic mass units.

The Incos data system consists of a Nova 3/12 memory, sixteen bit word central processing unit with 700 nanosecond cycle time. This computer stores the data of the 129 EPA listed priority pollutants.

Known compounds were added to the coal wastewaters to evaluate the accuracy of the analysis.

Details of the GC-MS identification procedures can be found in Appendix A.

SECTION 5

EXPERIMENTAL PROCEDURE

PRELIMINARY SAMPLE TREATMENT

Sample Acquisition and Storage

The following two wastewater samples, representative of coal gasification and liquefaction processes, were obtained:

1. Scrubber water from a coal hydrocarbonization process, derived from a gasification plant fluidized bed operation at 300 psi and 1035°F. (Oak Ridge Division of Union Carbide Corporation). It will be referred to in this report as water sample No. 1.

2. Recycle process water No. 1511, from a coal liquefaction plant. PAMCO at DuPont, Washington. It will be referred to in this report as water sample No. 2.

These two wastewaters were stored in closed vessels at 4°C.

ANALYTICAL PROCEDURE

The schematic diagrams of analytical procedure for organics classification is represented in Figure 4 and consists of the following steps:

Physical and Chemical Properties Analysis

The raw wastewater was filtered through Millipore submicron filters (0.22μm) to remove grease and large suspended solids, in order to study the soluble species.

The samples were examined to determine both the organic and the inorganic loads, as well as other water quality parameters, by Standard Methods (Standard Methods for the Examination of Water and Wastewater, 14th edition, American Public Health Association, 1976)[8]. Results are shown in Table 2.

Both samples have pH values of 9.1, and in comparison to most industrial waste effluents and sewage, contain high COD and TOC values due to their heavy loads of organic and inorganic chemicals. Low BOD_5 values may be due to toxic chemicals in the sample which could cause failure of acclimation of bacteria. High concentrations of phenol exist in both water samples examined.

Both samples would be expected to have high NH_3-N concentrations; however, due to interference by high concentrations of bicarbonate salts

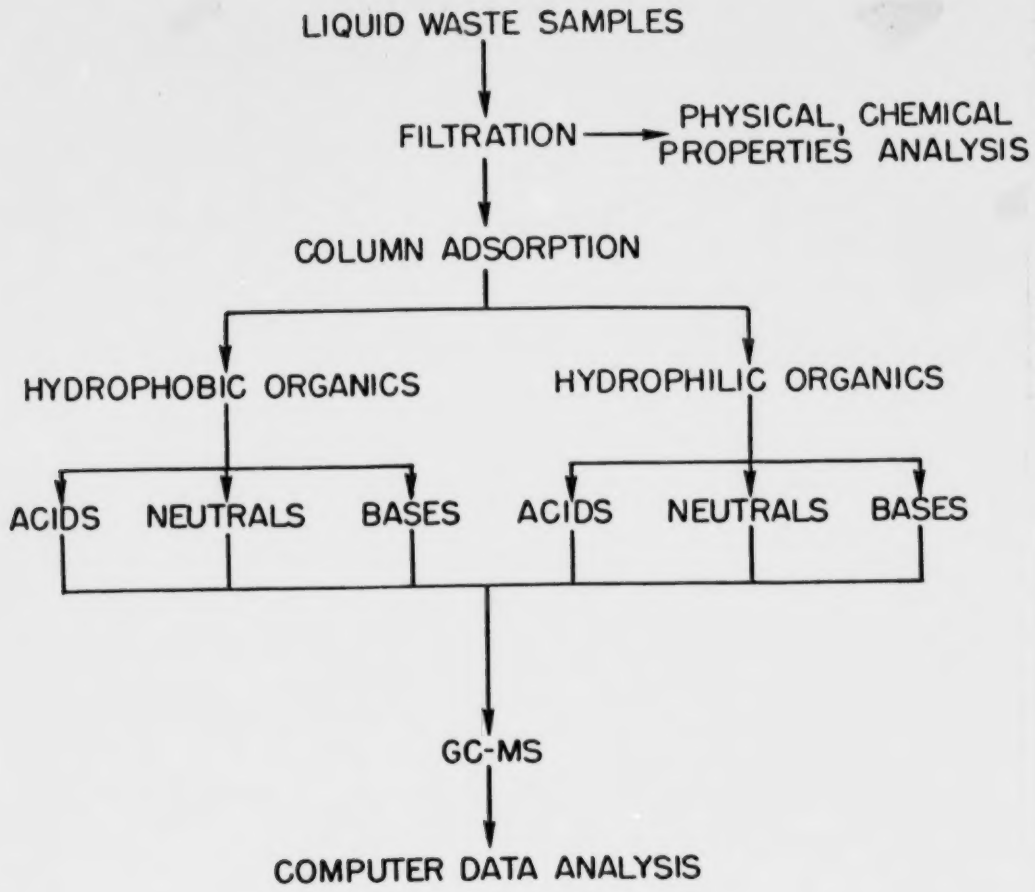


Figure 4 Schematic Diagram of Analytical Procedure.

Table 2. ANALYSIS OF CHEMICAL PROPERTIES IN TWO COAL WASTEWATER SAMPLES (mg/l).

Parameters	Sample 1	Sample 2
pH	9.1	9.1
TOC (Total Organic Carbon)	6,250	3,510
COD (Chemical Oxygen Demand)	18,400	12,700
BOD_5 (Biochemical Oxygen Demand)	<10	<10
Phenols	10,000	6,000
NH_3-N	3,000	5,000
Alkalinity as $CaCO_3$	3,210	3,360
Hardness	50	3
Conductivity (25 C)	5,300 µmhos/cm	4,700 µmhos/cm
Total Solids	852	800
Dissolved Solids	436	800
Suspended Solids	416	<4
Boron	0.8	8.0
Chloride	710	36
Fluoride	<1	<1
Nitrate	<1	<1
Phosphate	0.76	1.0
Silica	<2	<2
Sulfate	960	1,800
Al	<10	<10
As	<0.05	<0.05
Ba	<5	<5
Be	<0.2	<0.2
Cd	0.07	0.06
Ca	3.3	0.4
Cr	0.12	0.12
Co	<0.06	0.1
Cu	0.05	0.02
Fe	0.27	0.12
Pb	<0.1	0.36
Mg	3.4	0.03
Mn	0.18	0.005
Hg	0.01	0.01
Mo	0.6	<0.5
Ni	<0.6	0.26
Se	1.3	1.2
Ag	0.75	0.08
Na	12	5
Sn	3.5	5.0
V	<100	<100
Zn	0.05	0.03

(NH_4HCO_3), the expected values of NH_3-Nitrogen were not observed. Boron, chloride, sulfur as sulfate, aluminum, barium, calcium, magnesium, selenium, sodium, tin and vanadium are the major elements in both waters.

Organic Analysis

Column Adsorption Separation

The first classification step was the separation of the organic component into hydrophobic and hydrophilic compounds on Amberlite XAD-8 macroreticular resin. Further classification was based upon acid base characteristics. Hydrophobic acids and bases were desorbed by aqueous alkali (0.5 N NH_4OH) and acid (0.1 N HCl), respectively. Hydrophobic neutrals were eluted with methanol. Hydrophilic acids and bases were adsorbed on cation and anion exchange resin and eluted in 0.5 N NH_4OH. Hydrophilic acids were concentrated on OH^--form AG MP-1 anion exchange resin and eluted with 0.5 N HCl. Hydrophilic neutrals passed through all columns (Figure 5).

The XAD-8 resin was supplied as an industrial grade product (20-40 Tyler mesh) which was purified by first rinsing with 0.1 N NaOH, 0.1 N HCl, and then by Soxhlet extracting for 24 hours successively using acetonitrile, ethyl ether, and methanol. The resin was then packed in a column rinsed with distilled water, and tested for organic compounds prior to usage.

The AG MP-50 and AG MP-1 resins were washed successively by 1N HCl, 1N NaOH, and then Soxhlet extracted successively for 24 hours in methanol, methylene chloride, and n-pentane prior to use as column packing. Test samples of model compounds were made and the extent of the separation was noted prior to usage.

One liter of water sample No. 1 was diluted to 3 liter volume with distilled water and passed through a 300 ml bed (3 bed volume) XAD-8 resin column. The flow rate of the sample was 10 ml/min. The column was then eluted with 500 ml 0.1 N HCl, 0.5 N NH_4OH, and CH_3OH to collect HO base, acid, and neutral compounds, respectively. The aqueous effluents were passed through a column of H^+ form cation exchange resin (BioRad AG MP-1) to separate HI components. HI based were collected by eluting with 500 ml 0.5 N NH_4OH. Acids were recovered by eluting with 2.0 N HCl. HI neutrals remained in the aqueous effluent. The water sample No. 2 was also separated via the same procedures. However, it was diluted with distilled water by the ratio of 1:1. This is because the total organic carbon concentration of water sample No. 2 is about one half of the first. The purpose of dilution is to reduce solute-solute interactions at high solute concentrations.

Total Organic Carbon Analysis for Separated Fractions

There are six separated fractions which result for each sample subjected to the column absorption separation process. The organic components in these fractions are classified as hydrophilic acid, base, neutral and hydrophobic acid, base, and neutral compounds. Total organic carbon

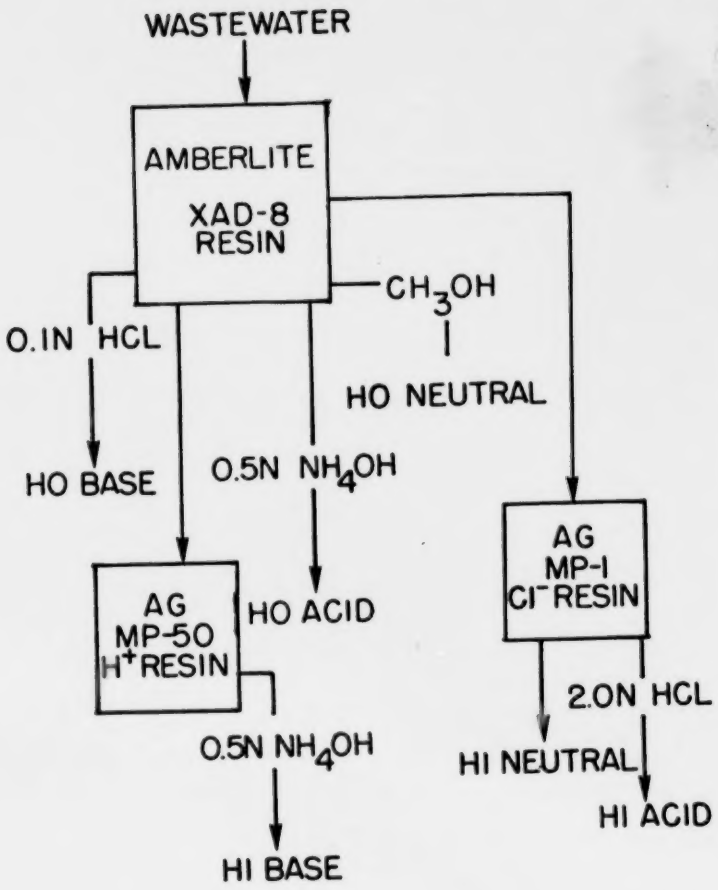


Figure 5. Flow Diagram of Column Adsorption to Separate Organics in Coal Process Water.

concentration of these fractions was detected by using a Dohrmann Envirotech DC-50 Model TOC analyzer. Preliminary data of TOC distribution among these fractions are shown in Table 3.

All the fractions were in aqueous solution except the HO neutral fraction, which was eluted with CH_3OH from the column. The HO neutral fraction also contained some water and inorganic salts which were introduced by the columns. Benzene was then used to recover the pure organic component in the HO neutral fraction.

The TOC data indicated that the HO neutral fraction contained the highest organic concentration and it should be noted that this is higher than the calculated concentration, since other fractions might contain some CH_3OH. Since the HO neutral fraction was not readily dissolved back into water, it was not possible to measure the TOC value directly. The values were approximated from GC peaks of the solvent and solute concentration. Other alternative methods also will be used in the future.

Infrared Spectrometry Study of Separated Fractions

HO neutral fractions of sample No. 1 and No. 2 were subjected to IR analysis for functional group studies, involving the use of a Beckman AccuLab 6 Infrared Spectrophotometer with liquid cells. The IR spectra of samples No. 1 and No. 2 are shown in Figures 6 and 7, respectively. The IR absorption bands of functional groups in the spectra were assigned as shown in Table 4. From the IR study of the HO neutral fractions, the major organic compounds in the two samples are quite similar. A strong presence is indicated for substituted aromatic hydrocarbons, phenolic compounds and aldehydes.

Preliminary Mass Spectrometry Study

A preliminary mass spectrometry study of the HO neutral fraction samples was made. In order to favorably separate the compounds on a suitable GC column, benzene was first removed from the HO neutral fraction. The remaining fraction was then found suitable for GC-MS analysis.

A Hewlett-Packard Model 5985 gas chromatographic mass spectrometer was used. Samples were introduced via the direct probe inlet accompanied with CH_2Cl_2. The mass spectra of the HO neutral fraction in water samples No. 1 and No. 2 are shown in Figures 8 and 9, respectively. The range of high abundance for water sample No. 1 is between 100 to 150. The spectrum indicates that the mass of organic compounds in the samples is under 300 and most likely between 100 and 200.

Since the samples were mixtures of organic compounds, they were separated through GC and then identified by MS with computerized spectra matching.

Gas Chromatograph-Mass Spectrometry Analysis

The separate organic fractions from coal process wastewater were sub-

TABLE 3. PERCENTAGE OF TOTAL ORGANIC CARBON DISTRIBUTION IN SEPARATED FRACTIONS

Separated Fraction	% of origin in-put TOC*	
	No.1	No.2
HI acid	2.7	3.4
HI base	2.4	6.8
HI neutral	10.7	15.2
HO acid	9.4	14.5
HO base	7.1	12.6
HO neutral	48**	40**

*The original input TOC for No.1 and No.2 are 2083 ppm, 1755 ppm, respectively.

**Values approximated from GC peaks of solvent.

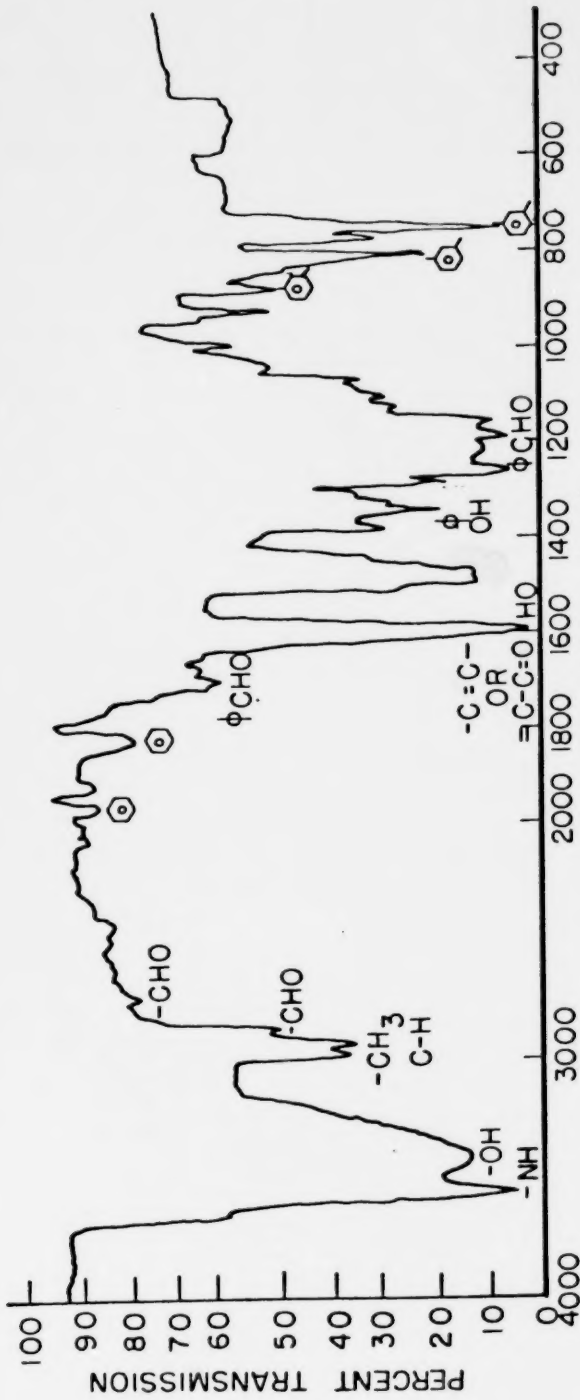


Figure 6. IR Spectrum of HO Neutral Fraction of Sample No.1

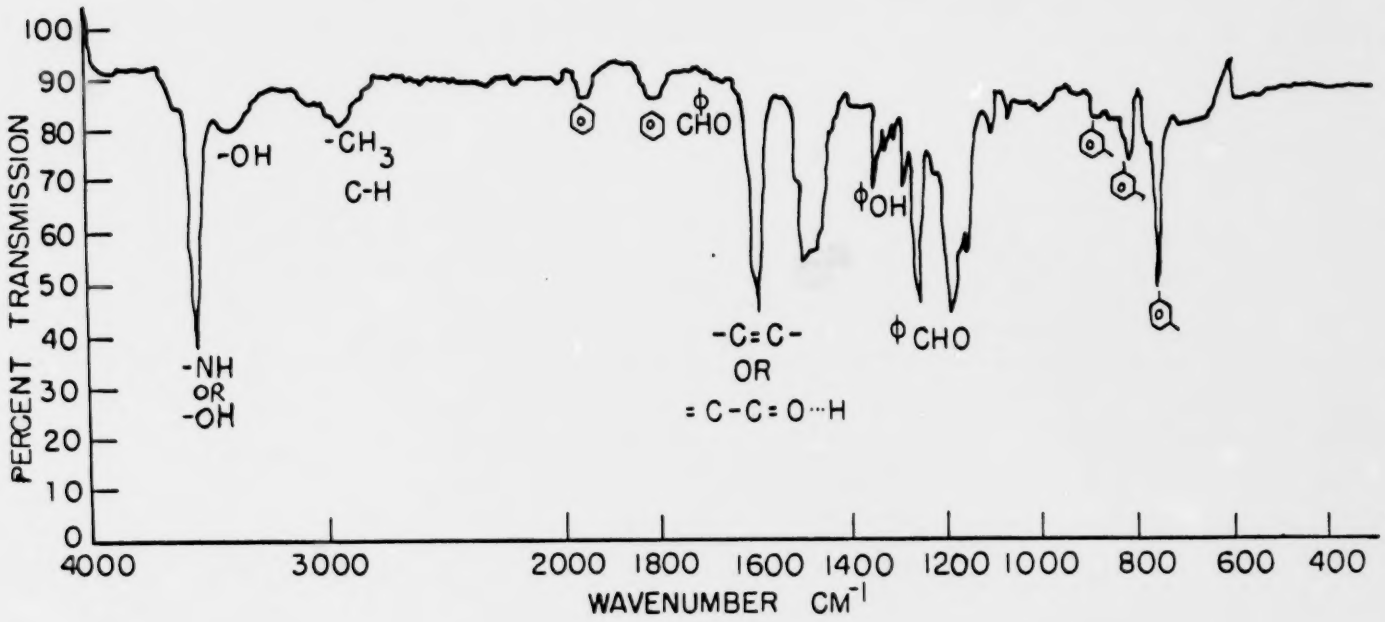


Figure 7. IR Spectrum of HO Neutral Fraction of Sample No.2

Table 4. IR ABSORPTION OF ORGANIC COMPOUNDS IN SAMPLES NO. 1 AND NO.2 FROM COAL WASTEWATERS:

Absorption (cm^{-1} wavenumber)	Structural Assignment
3560	Intramolecular H-Bonded -OH groups
3400	Intermolecular H-Bonded -OH groups
2970, 2930	$-CH_3$ Alkane modes C-H stretching
2870, 2740	-CHO Aldehyde C-H stretching
1950, 1800, 880, 810, 750	Aryl C-H out-of-plane deformation
1600	-C=C- aromatic double-bond stretching
	or
	=C-C=0···HO carboxylic group
1450	C-H bending
1340	phenol
1700, 1260	ϕ-CHO aromatic aldehyde

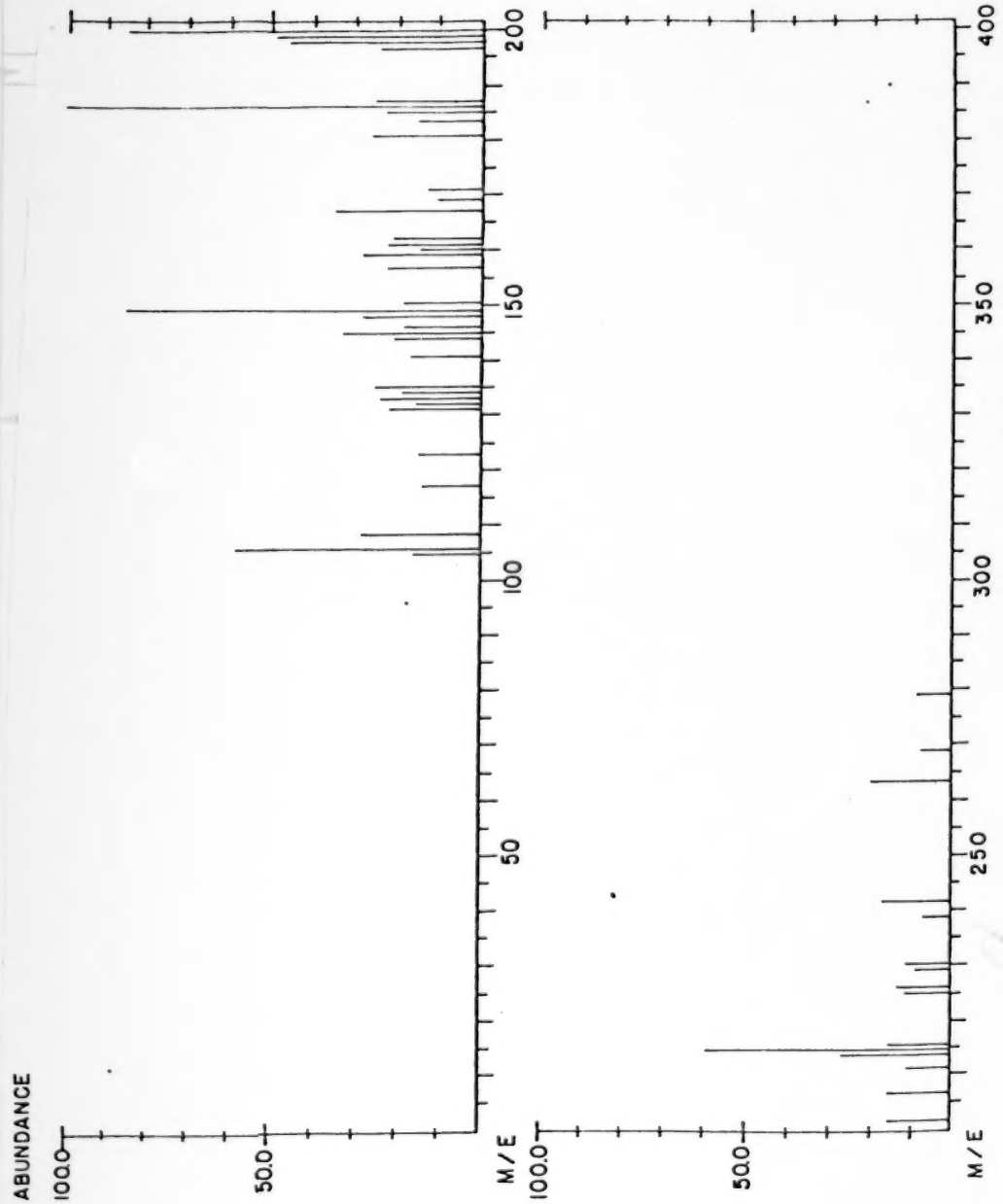


Figure 8. Mass Spectrum of HO Neutral Fraction of Sample No.1.

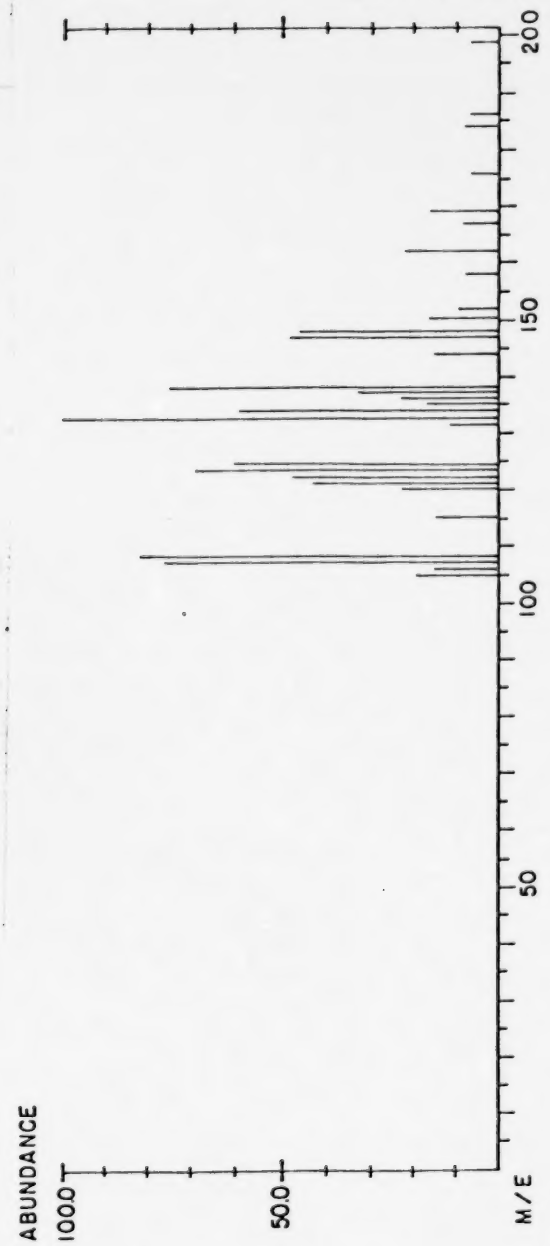


Figure 9. Mass Spectrum of HO Neutral Fraction of Sample No.2.

jected to GC-MS analysis. As stated previously, these fractions are classified as HO acid, base, neutral and HI acid, base, and neutral.

All the fractions were in aqueous solution except the HO neutral fraction, which was eluted with CH_3OH through the column. Benzene was used to recover the pure organic component in HO neutral fraction. Samples of HO neutral fraction then were diluted to 1 ml in benzene for GC-MS analysis. All other fractions were extracted by dichloromethane (CH_2Cl_2). After phase separation occured, a 2.0 µl aliquot of the CH_2Cl_2 was analyzed by GC-MS. The GC-MS operating parameters are summarized in Table 5.

The GC column elution fractions passed into the ion volume of the mass spectrometer which automaticlly scans mass range equivalent to a GC signal. Ion current was then amplified and plotted against the spectrum scan time base. The computer stores the output and plots a reconstructed ion chromatogram (RIC) of total ion amplitude versus the spectrum number. The RIC of organic compounds in one fraction as well as the mass spectra of individual GC peaks in that fraction are included in the Appendix A.

Computer Analysis of GC-MS Data to Identify Organic Compounds

Identification was accomplished by measuring relative retention time in GC and comparing the mass spectrum with data stored in the reference library with a specific m/e value. The mass spectra in the library were searched for those matching at least four of 16 largest peaks in the sample. They were then ranked according to their closeness of fit to the sample spectrum. An example of computer analysis is included in the appendix.

Quantitative Analysis of Priority Pollutants

Four of the 12 separated fractions had undergone analysis for priority pollutants. (The EPA priority pollutant list is shown in Appendix B). The selected fractions were: HO neutral fraction in sample No. 1, HI neutral fraction in sample No. 2, HO base fraction in sample No. 2, and HI acid fraction in sample No. 2.

Samples were analyzed by GC-MS method using the following procedure:

1. liquid-liquid extraction using methylene dichloride as solvent
2. evaporation of the solvent to concentrate sample
3. injection of the sample into GC-MS

The results of quantitative analysis are represented in Table 21 to 23 of Section 6.

MUTAGENIC POTENTIAL ASSESSMENT OF COAL LIQUID WATER EXTRACTS

Origin

Coal liquids are the unrefined end products from coal liquefaction processes. They contain high percentages of aromatic and polyaromatic compounds and saturated paraffins. Characterization of this synthetic crude oil by

Table 5. GC-MS Operating Parameters.

Instrument:	Finnigan 3200 coupled to Incos data system
Column:	5' in length, 1.8 m x 2 mm in width, glass, 3%SP225 on 100-120 Supelcoport
Temperature:	90°C to 200°C @ 10/min.
Separator Temperature:	250°C
Emission Current:	450 microamp
Preamp Range:	10^{-7} amp/volt
Electron Multiplier Voltage:	1600 volts
Manifold Temperature:	80°C
Electron Energy:	70 ev

capillary column GC-MS technique was done by Bertsch and Anderson(1976).[10] The major components are homologs of substituted naphthenes, aromatic compounds, indanes and naphthalenes (Table 6). A large portion of these chemicals are potentially toxic to the environment. Biological studies indicated that certain fractions in coal liquids are mutagenic (Rubin, et al., 1976)[9].

To investigate any mutagenic effect from water soluble or water miscible portions of coal liquids, four kinds of coal liquid samples from different commercial coal liquefaction demonstration projects were obtained and are listed in Table 7. The process for treating coal liquids proceeded as follows: samples were transferred in capped glass vessels (if the liquid was a semi-solid at room temperature, then heat soaking at 50°C overnight was required) in which ceramic balls were placed. Ball-milling was continued for three days, at which time the aqueous layer was separated. Anisole was used as a solvent for the continuous liquid-liquid extraction of the aqueous layer. Anisole was allowed to evaporate, and the organic compounds extracted by the solvent from the aqueous phase were isolated in this way. The weight percentage of organics from coal liquid samples after removal of anisole are shown in Table 8. The organics were dissolved in dimethyl sulfoxide, DMSO, for the Ames Test mutagenicity test.

Mutagenicity Test for Coal Liquid Water Extracts

After removing anisole by vacuum evaporation, the concentrated organics were ready for the mutagenic test (page 53).

In this test, a small sample of about 1 mg of the suspected mutagen is placed in the center of a petri plate that has been seeded with a lawn of bacteria. If the mutagen can cause the particular mutation to revert in an occasional bacterium, it will enable that bacterium to grow and form a colony. Therefore, a circle of colonies will appear around the spot of mutagen after a day and a half of incubation. For this purpose, many histidine auxotrophic strains of Salmonella typhimurium are used, because they can be reverted to histidine prototrophy by the suspected mutagen sample.

TABLE 6. IDENTIFICATION OF MAJOR COMPOUNDS IN A COAL-DERIVED FLUID (Ref. 10)

Peak No.	Compound	Peak No.	Compound
1	Ethane	80	*o*-Xylene
3	Chloromethane	82	C_9H_{18}
4	C_4H_{10}	84,85	Methylethylcyclohexane
6	Pentane	87	Isopropylbenzene
7	Dichloromethane	88	Propylcyclohexane
9	2-Pentene	90,91	Methylethylcyclohexane
10	2-Methylpentane	92,93	Propylcyclohexane
11	3-Methylpentane	95,96	*n*-Propylbenzene
12	*n*-Hexane	97	1-Methyl-3-ethylbenzene
14	Methylcyclopentane	98	1-Methyl-4-ethylbenzene + *trans*-hexahydroindan
15	C_7H_{14}		
17	C_7H_{14}	99	1,3,5-Trimethylbenzene + methylnonane
18	Benzene		
19,20	Cyclothexane	100	1-Methyl-2-ethylbenzene
21	Dimethylpentane	101	1-Methyl-2-ethylbenzene
23	Cyclohexene	102	$C_{10}H_{20}$+ C_4-alkylcyclohexane
24	C_7H_{16}	103	1,2,4-Trimethylbenzene
25	C_7H_{14}	104	*cis*-Hexahydroindan
27	Dimethylcyclopentane	105	C_4-Alkylcyclohexane
28	C_8H_{16}	106	$C_{10}H_{22}$
29	C_7H_{16}	107	C_3-Alkylcyclohexane
31	Dimethylpentane	108,109	$C_{10}H_{22}$ + C_4-alkylcyclohexane
32	Dimethylpentene	110	$C_{10}H_{20}$
34	3-Ethyl-1-pentene	111	$C_{10}H_{18}$
35	3-Ethyl-2-pentene	112	1,2,3-Trimethylbenzene + $C_{10}H_{18}$
36	C_2-Alkylcyclopentane	113	$C_{10}H_{18}$ + C_4-alkylbenzene
37	C_8H_{18}	115	Indan
38	Methylhexadiene + C_8H_{18}	117	*sec.*-Butylcyclohexane
39-41	Toluene	118	*n*-Butylcyclohexane
43	Methylhexadiene	119	C_4-Alkylcyclohexane
44	2,5-Dimethylhexane	120	$C_{10}H_{18}$
45	C_8H_{18}	121	C_4-Alkylbenzene
46	C_8H_{18}	122	C_4-Alkylbenzene
48-50	Dimethylcyclohexane	124,125	C_4-Alkylbenzene
51,52	Methylethylcyclopentene	126	C_4-Alkylcyclohexene + $C_{10}H_{18}$
53	Dimetyhlcyclohexane	127	*trans*-Decahydronaphthaleno
54	Dimethylcyclohexane	128	C_4-Alkylbenzene + $C_{10}H_{18}$
56	Dimethylcyclohexane	129	*cis*-Decahydronaphthalene
59	Methylethylcyclopentane	130	C_4-Alkylbenzene
60	Dimethylcyclohexene	131	$C_{11}H_{24}$
64-66	C_3-Alkylcyclopentane	134	C_5-Alkylbenzene
67	C_8H_{16}	135	$C_{10}H_{18}$ + $C_{11}H_{22}$
68	C -Alkylcyclopentane	136	Methyldecane + nor-undecane
69	Ethylbenzene	137	Methyldecahydromaphthalene
71	Trimethylcyclohezane	138	Dimethylindan
72	*p*-Xylene	140	Ethylstyrene + C_5-alkylbenzene + 5-methylindan
73	*m*-Xylene		
74	C_5H_{14}	141	Methyldecahydronaphthalene

TABLE 6 (continued)

Peak No.	Compound	Peak No.	Compound
142	C_2-Alkylindan + C_5-alkylbenzene	182	C_3-Alkylindan
143	C_5-Alkylbenzene	183	C_3-Alkylindan
144	5-Methylindan	184	$C_{13}H_{28}$
145	4-Methylindan	185	C_3-Alkylindan
147	C_5-Alkylbenzene	186	Methyltetrahydronaphthalene + C_3-alkylindan
148	Tetrahydronaphthalene	187	2-Methylnaphthalene
150	C_5-Alkylbenzene + methyldecahydronaphthalene	188	C_3-Alkylindan
151	C_5-Alkylbenzene	189	C -Alkyltetrahydronaphthalene
153	C_5-Alkylbenzene	190	1-Methylnaphthalene
154	Naphthalene	191	*n*-Tridecane
155,156	C_2-Alkylindan	193	Cyclohexylcyclohexane
157	C_2-Alkylindan	194,195	Dimethyltetrahydronaphthalene
158	C_2-Alkylindan	196	Ethyltetrahydronaphthalene + C_7-Alkylbenzene
159	C_2-Alkylindan	197	C_3-Alkylindan
160	C_2-Alkylindan	198	C_3-Alkylindan
161	4,1-Dimethylindan	199	C_3-Alkylindan
162	C_5-Alkylbenzene	200	C_2-Alkyltetrahydronaphthalene + methylcyclohexylhexane
163	*n*-Dodecane	201	C_2-Alkyltetrahydronaphthalene
164,165	Methyltetrahydronaphthalene	204	C_2-Alkyltetrahydronaphthalene
166	C_3-Alkylindan	205	C_2-Alkyltetrahydronaphthalene
167	C -Alkylbenzene	206	C_2-Tetrahydronaphthalene
168	C_6-Alkylbenzene + $C_{13}H_{28}$	208	$C_{13}H_{18}$
169	Methyltetrahydronaphthalene	210	$C_{13}H_{18}$
170,171	C_3-Alkylindan	212	$C_{13}H_{18}$
172	C_3-Alkylindan	213	C_2-Alkylnaphthalene + C -alkylindan + $C_{13}H_{28}$
173	C_2-Alkylindan	214	C_3-Alkylindan
174,175	C_6-Alkylbenzene	215	C_2-Alkylnaphthalene + $C_{13}H_{18}$
177	C_3-Alkylindan	216,217	C_2-Alkylnaphthalene + $C_{13}H_{18}$
178,179	Methyltetrahydronaphthalene + $C_{17}H_{24}$	218	$C_{13}H_{18}$
181	C_3-Alkylindan		

TABLE 6 (Continued)

Peak No.	Compound	Peak No.	Compound
219	C_2-Alkylnaphthalene	241	$C_{14}H_{20}$
220	C_2-Alkylnaphthalene	243	C_3-Alkylnaphthalene
221	C_2-Alkylnaphthalene + $C_{13}H_{16}$	247	C_2-Alkylnaphthalene
222	$C_{13}H_{16}$	249	Fluorene
223	$C_{13}H_{18}$	255	Hexadecane
224	$C_{13}H_{18}$	260	$C_{17}H_{36}$
225	C_3-Alkylnaphthalene	262	Octahydrophenanthrene
226	$C_{13}H_{18}$	263,264	Methylfluorene
229	C_3-Alkyl-1,2-dihydronaphthalene	265	n-Heptadecane
230	$C_{14}H_{20}$ + $C_{15}H_{32}$	268	$C_{18}H_{38}$
231	Diphenylmethane	269	Methoxyfluorene
232	$C_{13}H_{18}$	273	n-Octadecane
235	$C_{14}H_{20}$	274	Dimethylfluorene
237	C_3-Alkylnaphthalene	277	n-Nonadecane
238	n-Pentadecane	278	n-Eicosane
240	$C_{14}H_{20}$	279	n-Heneicosane

TABLE 7. PROPERTIES OF COAL LIQUIDS USED

Description	A	B	C	D
Prod. Temp. (^{o}C)	450	450	450	455
Pressure (psig)	1766	1499	4000	2390
Analyses				
%C	87.37	87.94	86.67	88.45
%H	7.37	6.77	8.38	5.51
%N	0.84	1.37	0.93	1.26
%S	0.17	1.26	0.09	0.19
%O	4.25	1.40	3.24	4.30
%Ash	0.10	4.75	0.69	0.29

Note: The coal liquid samples were obtained from different demonstration projects of coal liquefaction processes.

TABLE 8. WEIGHT PERCENTAGE OF WATER SOLUBLE ORGANICS FROM COAL LIQUID SAMPLES

Code No.	A	B	C	D
Total Sample wt (gm)	72.4	63.9	125.8	147.3
Water Soluble Organics wt (gm)	1.34	0.35	1.07	0.99
wt% of Water Soluble Organic	1.85	0.54	0.85	0.67

SECTION 6

RESULTS AND DISCUSSION

GENERAL STATEMENT

The preliminary qualitative and quantitative analyses have been completed. The major organic contaminants in the coal liquid processing wastewater samples identified by the current investigation are:

a) hydrophobic acid fraction--phenolic compounds, such as phenol, cresol, xylenol.

b) hydrophobic neutral fraction--PAHs such as naphthalene, anthracene, pyrene, benzo(a)anthracene, chrysene, fluoranthene, biphenyl.

c) hydrophobic base fraction--azo-aromatics and nitrogen base compounds, such as diphenylhydrazine, indole, nitrobenzene, pyridine quinoline, benzamine.

d) hydrophilic acid fraction--phenolic compounds, aromatic acids, and volatile acids, such as phenol, cresol, xylenol, carboxylic acid, benzoid acids, fatty acids.

e) hydrophilic neutral fraction--cyclic polar compounds, such as ethylphthalate, benzylphthalate, cyclopentenone.

f) hydrophilic base fraction--methoxybenzene.

Qualitative results are presented in Table 9 to 20. A separate quantitative analysis for compounds appearing on the EPA priority pollutant list is presented in Tables 21 to 24.

As can be observed, the results from qualitative and quantitative analyses were not matched closely. The reason for this discrepancy is due to several differing conditions employed in the two analyses. In the quantitative GC analysis, the column temperature was higher than that of the qualititative GC analysis. Therefore, more high boiling point PAHs were identified. Furthermore, the computer system only compared spectra for the EPA priority pollutants in the quantitative analysis, while in qualititative analysis, it searched among thousands of organic compounds. The predominant species, including phenols and cresols, were found in both analyses.

TABLE 9. COMPOUNDS IDENTIFIED FROM HO NEUTRAL FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	M. W.	COMPOUND
77	91	92	methylbenzene
131	43	88	ethyl acetate
193	108	108	methoxybenzene
244	94	94	phenol
264	107	108	2-methylphenol
286	107	108	3-methylphenol
303	107	122	3,5-dimethylphenol
315	107	122	2,5-dimethylphenol
324	107	122	3,4-dimethylphenol
331	121	136	4-(1-methylethyl)-phenol
335	121	136	2-ethyl-5-methylphenol
343	121	136	2-ethyl-4-methylphenol
352	121	136	4-ethyl-2-methylphenol
382	133	134	3,4-dimethylbenzaldehyde
394	133	148	pentamethylbenzene
451	144	144	3-phenylfuran
506	170	170	(1-1-biphenyl)-3-ol

TABLE 10. COMPOUNDS IDENTIFIED FROM HO BASE FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
76	93	129	aniline hydrochloride
99	106	107	4-melhylaniline

TABLE 11. COMPOUNDS IDENTIFIED FROM HO ACID FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
52	55	98	cyclohexanone
74	94	94	phenol
98	107	108	2-methylphenol
113	107	108	3-methylphenol
135	107	122	2,5-dimethylphenol

TABLE 12. COMPOUNDS IDENTIFIED FROM HI NEUTRAL FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	M. W.	COMPOUND
49	91	106	1,2-dimethylbenzene
93	105	140	1-chloro-2,4-dimethylbenzene
124	96	96	3-methyl-2-cyclopenten-1-one
207	57	184	4,7-dimethylundecane

TABLE 13. COMPOUNDS IDENTIFIED FROM HI BASE FRACTION IN WATER SAMPLE NO. 1

GS SCAN NO.	BASE M/E	M. W.	COMPOUND
77	94	94	phenol
91	105	140	1-chloro-2,4-dimethylbenzene
146	186	186	1-bromo-2-methoxybenzene
205	57	184	5-methyl-5-propylnonane

TABLE 14. COMPOUNDS IDENTIFIED FROM HI ACID FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
54	74	130	methyl hexanoic acid
47	91	106	5-(1-methly)-1,3-cyclopentadiene
77	94	94	phenol
105	107	108	3-methylphenol
116	105	136	methyl benzoic acid
163	59	174	dimethyl hexanedioc acid
169	104	164	methylbenzenepropanoic acid
177	133	164	3,5-dimethyl methylbenzoic acid
204	57	184	3-ethyl-3-methyldecane
234	163	194	dimethyl-1,2-benzenedicarboxylic acid

TABLE 15. COMPOUNDS IDENTIFIED FROM HO NEUTRAL FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
167	108	108	methoxybenzene
224	94	94	phenol
254	107	108	2-methylphenol
272	107	108	bicyclo(2,2,1)hepta-2,5-diene
290	107	122	2-ethylphenol
295	122	122	2,5-dimethylphenol
306	107	122	2,3-dimethylphenol
318	107	122	3,4-dimethylphenol
326	121	136	4-(1-methylethyl)-phenol
331	121	136	2-ethyl-5-methylphenol
339	107	136	2-ethyl-4-methylphenol
357	135	150	2-(1,1-dimethylethyl)-phenol
379	133	134	3,4-dimethylbenzaldehyde
391	133	148	2-(2-methyl-2-propenyl)-phenol
429	123	138	1,1,2-trimethyl-3-cyclopropane
504	170	170	(1,1-biphenyl)-3-ol
606	186	186	(1,1-biphenyl)-2,2-diol

TABLE 16. COMPOUNDS IDENTIFIED FROM HO BASE FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
37	93	93	methylpyridine
48	107	107	2,6-dimethylpyridine
54	93	123	ethylpyridine
58	108	108	phenylhydrazine
65	107	107	2,4-dimethylpyridine
84	93	93	aniline
86	93	93	4-methylpyridine
112	106	143	2-melhylaniline hydrochloride
129	132	147	2-methyl-2,3-dihydro-IH-indole
141	106	121	5-methyl-3-ethylpyridine
160	118	133	5,6,7,8-tetrahydroquinoline
171	129	129	quinoline
187	143	143	2-methylquinoline
196	132	133	1,2,3,4-tetrahydroquinoline

TABLE 17. COMPOUNDS IDENTIFIED FROM HO ACID FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
56	108	108	methoxybenzene
75	94	94	phenol
145	63	186	1-bromo-2-methoxylbenzene
162	94	138	2-phenoxyethanol

TABLE 18. COMPOUNDS IDENTIFIED FROM HI NEUTRAL FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
36	41	98	2-methyl-2-pentenal
57	108	108	methoxy benzene
43	91	106	1,2-dimethyl benzene
89	105	140	1-chloro-2,4-dimethyl benzene
115	105	140	1-chloromethyl-3-methyl benzene

TABLE 19. COMPOUNDS IDENTIFIED FROM HI BASE FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M.W.	COMPOUND
58	108	108	methoxy benzene
89	105	140	1-chloro-2,4-dimethyl benzene

TABLE 20. COMPOUNDS IDENTIFIED FROM HI ACID FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	M. W.	COMPOUND
45	91	106	ethyl benzene
78	94	94	phenol
204	57	226	5-propyl tridecane

TABLE 21. QUANTITATIVE ANALYSIS OF HO NEUTRAL FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	CONC.(µg/l)	COMPOUND
377	123	0.938	nitrobenzene
403	128	2.750	naphthalene
711	178	0.549	anthracent+phenathrene
632	149	0.136	diethyl phthalate
766	149	282.354	di-n-butyl phthalate*
846	202	0.587	pyrene
939	167	59.920	bis(2-ethylhexyl)phthalate*
967	228	0.009	benzo(a)anthracene+chrysene
273	74	1082.800	N-nitrosodimethylamine
630	77	0.149	1,2-diphenylhydrazine
711	178	0.549	anthracene+phenanthrene
823	202	0.014	fluoranthene
919	149	1.154	butyl benzyl phthalate
967	228	0.009	benzo(a)anthracene+chrysene

* Contaminate

TABLE 22. QUANTITATIVE ANALYSIS OF HI NEUTRAL FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	CONC.(µg/l)	COMPOUND
633	149	0.067	diethyl phthalate
765	149	579.699	di-n-butyl phthalate*
841	202	0.667	pyrene
939	167	2.429	bis(2-ethylhexyl)phthalate*
920	149	0.474	butyl benzyl phthalate

* Contaminate

TABLE 23. QUANTITATIVE ANALYSIS OF HI BASE FRACTION IN WATER SAMPLE NO. 2

GC SCAN NO.	BASE M/E	CONC.(µg/l)	COMPOUND
366	123	0.193	nitrobenzene
710	178	0.496	anthracene + phenanthrene
588	163	0.725	dimethyl phthalate
765	149	472.543	di-n-butyl phthalate*
939	167	14.577	bis(2-ethylhexyl) phthalate*
632	77	1.786	1,2-diphenylhydrazine
710	178	0.496	anthracene + phenanthrene
822	202	0.024	fluoranthene
919	149	0.927	butyl benzyl phthalate

* Contaminate

TABLE 24. QUANTITATIVE ANALYSIS OF HI ACID FRACTION IN WATER SAMPLE NO. 1

GC SCAN NO.	BASE M/E	CONC.(µg/l)	COMPOUND
135	135	2700×10^3	phenol
141	141	2700×10^3	cresol
170	170	200×10^3	cresol

PAHs

One of the principal carcinogenic classes of compounds which may be produced in coal conversion liquid wastes are PAH. The major PAH compounds already identified in coal liquid products are naphthalene, biphenyl, phenanthrene, benzo(a)anthracene, fluorene, and chrysene. The concentration levels of these compounds range from 18 to 413 ppm (Table 25).

In this study, most of those PAH compounds in wastewater samples except benzo(a)pyrene where identified and quantified. The benzo(a)pyrene is missing due to its boiling point, which is much higher than the GC column temperature (280°C).

The concentration of PAH compounds is in the µg/l or ppb range. However, the total quantity of each individual species in wastewater effluent will be at the gram level for daily outputs of an average pilot plant.

These quantities were estimated by multiplying each concentration by 5.45 liters per day and are shown in Table 26.

PHENOLS

The major organic portion of coal consists of phenolic compounds. Thus combined with this and the fact that for a typical pilot plant, the daily output of phenolics is about 10,000 kg, it is not surprising that phenols comprise up to 90 percent of the total organic content of process wastewater. Phenolic type compounds are found mostly in the acid fractions of both the hydrophobic and hydrophilic group.

Phenol, cresol, xylenol are the major phenolic type compounds identified which also appear on the EPA list of priority pollutants. Other phenolic compounds, including ethylmethyl phenol, ethyl phenol, and other polyalkyl phenols have also been found in the qualitative analysis. There are many isomers of these species in the coal wastewater samples. Also the hydroxyl-substituted biphenyls have been detected. Currently, GC-MS are the most effective tools to separate these isomers.

NITROGEN COMPOUNDS

The nitrogen content of most coals is generally below 2 per cent and is almost completely in cyclic structures. Some typical structures present in coal are shown in Figure 10 & 11. These compounds, and conversion process-generated species compose two of the principal environmentally hazardous compound classes to be found in coal process wastewaters, heterocyclic polyaromatic compounds and aromatic amines.

In the qualitative analysis, aromatic amines are identified in all base fractions. The heterocyclic species, mainly pyridine and quinoline type compounds, are found in the hydrophobic base fraction (Table 16).

The concentration levels of nitrogen compounds are in the ug/l or ppb

TABLE 25. QUANTITIES OF PAH IN A COAL-DERIVED LIQUEFACTION PRODUCT (Ref. 12)

PAH	Quantity (ppm)
naphthalene	347
2-methylnaphthalene	1325
1-methylnaphthalene	383
biphenyl	89
2,6-dimethylnaphthalene	328
1,3-dimethylnaphthalene	181
1,5- and/or 2,3 -dimethylnaphthalene	202
Benzo[α]pyrene	41
benzo[α]anthracene	18
phenanthrene	413
acenaphthalene	20
acenaphthene	61
fluorene	205
1-methylfluorene	152
2-methylfluorene	245
1-methylphenanthrene	107
9-methylanthracene	42
chrysene	98
2-methylchrysene	102
6-methylchrysene	64
3-methylchrysene	106

TABLE 26. ESTIMATED QUANTITIES OF PAHs IN COAL LIQUID WATER EXTRACTS

COMPOUND	CONCENTRATION (ug/l)	TOTAL QUANTITY Per day (gm)
Naphthalene	2.750	97.5
Anthracene	0.549	19.5
Phenanthrene	0.496	17.6
Pyrene	0.667	23.4
Benzo(a)anthracene	0.009	0.3
Chrysene	0.009	0.3
Fluoranthene	0.014	0.5

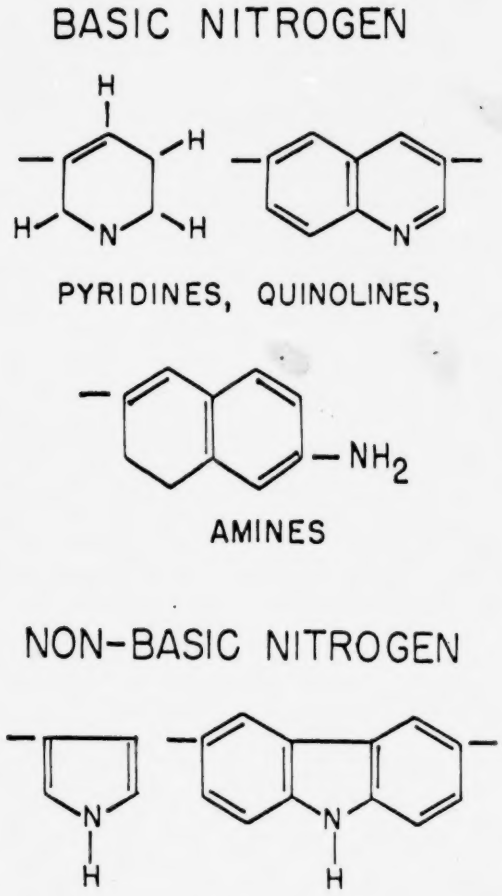


Figure 10. Typical Nitrogen Structure in Coal. (Ref. 11)

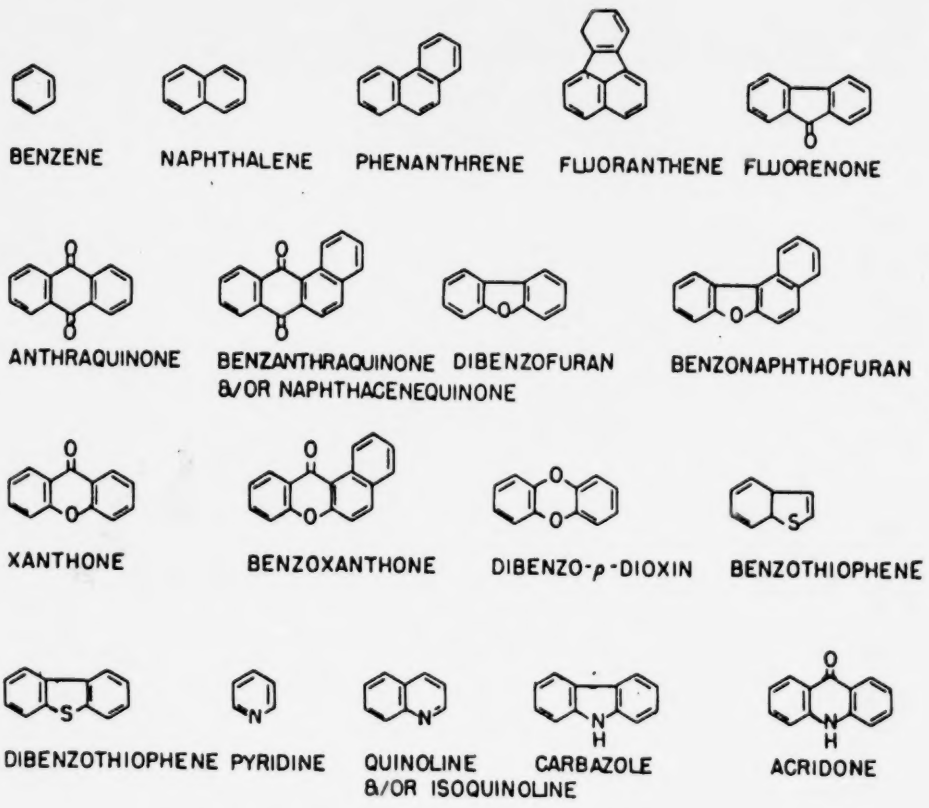


Figure 11. Compounds Identified as Indigenous to Coal

range, except in the case of N-nitroso-dimethylamine, which is a carcinogenic suspect and has a 1 ppm level, by quantitative GC-MS analysis (Table 21).

CHLORINATED HYDROCARBONS

Chlorinated benzenes were identified in hydrophilic fractions of samples by qualitative analysis (Table 12, 13, 18 and 19). However, they have not been found in the quantitative analyses by GC-MS. Their existence can probably be explained by the presence of inorganic chlorine in the organic coal matrix, and subsequent interaction with the aromatic ring systems during the industrial processing.

MUTAGENICITY ANALYSES OF COAL LIQUID WATER EXTRACTS

The preliminary results from qualitative tests are shown in Table 27. According to the Ames test, subsequent counts of revertant colonies of histidine negative Salmonella typhimurium strains were compared with those in the negative control. The sample is considered mutagenic if colony counts are greater than twice those of the negative control. The results from Table 27 indicated that in the presence of metabolic activity, strain TA 1537 and TA 1538 exhibited an increased rate or reversion by a factor of 2.0 to 3.0. Strain TA 1538 without metabolic activation also gave positive indication. These data label samples B and C as suspected mutagens. However, quantitative tests are required to study the correlation between mutagenicity and concentration of the suspect mutagens.

As mentioned earlier, a substance is considered mutagenic if the number of revertants with the test substance is two fold greater than the spontaneous reversion rate. The interpretation of quantitative results in Table 28 is based on testing the substance at 500 µg plate or the maximum non-inhibiting level. Discussion of the results is stated as follows:

1. Sample A - There was a minimal increase of a factor of 2.2 at 500 µg concentration over the background in the number of revertants with strain TA 1538. At concentration lower than 50 µg per plate, no appreciable increase was noted. In the case of TA 1535 with and without metabolic activation and TA 1537 with activation, there was some inhibition of reversion to prototrophy at the higher concentration of test substance.

2. Sample B - There was no mutagenic activity noted for strains TA 1353, TA 100, or TA 98, either with or without metabolic activation. With activation, strain 1538 exhibited an increased rate or reversion at 20 and 50 µg per plate by a factor of 2.0 and 4, respectively. At a higher concentration of 500 µg and a lower one of 10 µg, the increase in the number of revertants was minimal and below mutagenic levels. Strain TA 1537 had a consistent number of revertants about two fold higher than spontaneous at all concentrations of product. Since it is not

TABLE 27. QUALITATIVE TEST FOR MUTAGENICITY OF COAL LIQUID WATER EXTRACT SAMPLES

Histidine Reversions by Strain

Sample	TA98		TA100		TA1535		TA1537		TA1538	
	-	+	-	+	-	+	-	+	-	+
A	52	---	104	99	1	4	6	34	---	20
B	15	---	107	75	3	9	12	61	28	63
C	27	57	118	85	2	6	23	63	17	66
D	28	36	149	94	1	7	15	12	6	18
N/C	38	35	149	93	0	9	22	19	6	27

\- no metabolic activation (without rat liver microsome fraction)

\+ with rat liver microsome fraction

N/C negative control

TABLE 28. MUTAGENICITY TEST FOR COAL LIQUID WATER EXTRACTS

NUMBER OF REVERTANTS PER PLATE

Histidine Reversions by Strain

Sample	Concentration (ug)	TA 98		TA 100		TA 1535		TA 1537		TA 1538	
		-	+	-	+	-	+	-	+	-	+
A	10	12	46	69	109	21	16	7	30	14	26
	20	12	46	56	91	19	17	7	20	21	22
	50	15	45	66	87	22	21	5	20	15	33
	500	12	49	71	84	21	24	10	18	12	49
B	10	8	60	78	110	32	14	10	42	12	38
	20	10	45	69	85	31	18	10	42	19	90
	50	10	60	63	77	29	20	5	47	13	44
	100	0	41	60	79	26	16	2	44	16	26
C	10	15	51	80	129	25	23	5	32	24	37
	20	17	48	73	94	25	26	5	35	18	44
	50	10	51	85	97	23	19	5	41	12	14
	100	10	39	70	86	26	20	5	48	7	16
D	10	10	42	72	105	21	18	5	28	10	31
	20	13	38	85	111	24	26	7	23	14	28
	50	16	35	63	110	24	24	7	25	11	33
	500	20	35	65	76	17	18	5	17	11	32
N/C		35	48	85	100	23	19	6	20	17	23

\+ with metabolic activation (add rat liver microsome fraction)

\- no metabolic activation (without rat liver microsome fraction)

N/C negative control

a concentration dependent phenomenon, the explanation is probably not mutagenesis. There was a noticeable decrease in the number of revertants at higher concentration of test substance with strains TA 100, with and without metabolic activation.

3. Sample C - There was no mutagenic activity for strains TA 1535, TA 100, TA 1538, or TA 98. In the presence of metabolic activity, strain TA 1537 showed a minimal increase in the number of revertant colonies over the concentration range of test substance used. Strain TA 100, TA 1538, and TA 98 all exhibited a decrease in the numbers of revertants with increasing concentration of test substance (both with and without metabolic activation).

4. Sample D - There was no mutagenic activity observed with any of the tester strains of Salmonella typhimurium used.

From the above discussion, it is possible to conclude that both sample A and B are probable minimal mutagens for test strain TA 1538 after metabolic activation. Sample C is a probable minimal mutagen for strain TA 1537; metabolic activation by rat liver homogenate is necessary for this phenomenon. Sample D is not a mutagen in the present test system.

SUMMARY

Among the 129 priority pollutants listed by the EPA, 15 per cent or 20 compounds were quantitatively identified in samples of coal liquefaction and gasification process wastewaters. Phenolic compounds are the dominant species, with levels as high as 2700 ppm for phenol, and 200 ppm for cresol as the next most prevalent species. Most species are in the µg/l, or ppb range. One notable exception is a hazardous nitrogenous compound, N-nitroso-dimethylamine, which exists at 1 ppm. A summary of the concentration levels of identified priority pollutants is shown in Figure 12.

Since three of the four aqueous extracts from coal liquids exhibited mutagenicity, indicating possible toxicity, protective containment and monitoring of an accidental spill or runoff during a coal conversion operation is extremely important.

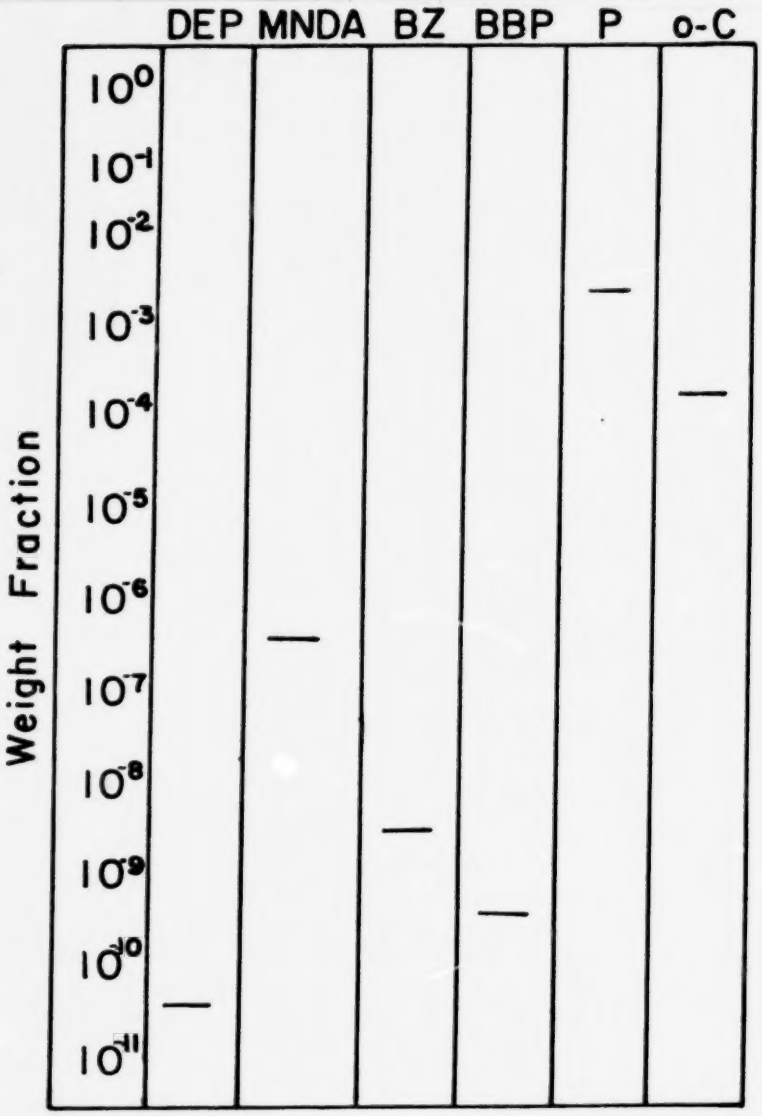


Figure 12. Summary of the Concentration of Identified Priority Pollutants in Raw Water Sample NO. 1.

Note:

DEP:	diethyl phthalate
MNDA:	N-nitroso-dimethylamine
BZ:	benzydine
BBP:	butyl benzyl phthalate
P:	phenol
o-C:	o-cresol

REFERENCES

1. Oak Ridge National Laboratory. Environmental, Health and Control Aspects of Coal Conversion: An Information Overview. ERDA Contract No. W-7405-eng-26, V. 1 & 2, 1977.

2. Rubin, E.S. and F.C. McMichael. Impact of Regulations on Coal Conversion Plants. Env. Sci. Tech. 9, (2), 112-117 (1975).

3. Victor, R.H.K., Environemntal Considerations Affecting the Development of a Coal Liquefaction Industry. ERDA No. E(49-18)-1752, 1977.

4. Yen, T.F., Proc. 1976 Coal Chemistry Workshop. SRI Menlo Park, CA., pp. 144-164, 1976. The Modified Structure of Wiser (1973)[11] has been built in Yen's laboratory. The configuration of folding, twisting and close approximation and interations of different modes of association has been demonstrated.

5. Peterson, M.R. Organic Constituents in Process Streams of a Solvent-Refining Coal Plant. Battelle Pacific Northwest Labs., BNWL-B-470, Richland, WA., 1975.

6. EPA. Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil, 65092-75-038, 1975, pp. 7-8.

7. Rohm and Hass Company, Summary Bulletin Amerlite Polymeric Adsorbtion. 1978.

8. American Public Health Associations. Standard Methods for the Examination of Water and Wastewater. 14th Ed. 1976.

9. Rubin, I.B..et al. Fractionation of Synthetic Crude Oil from Coal for Biological Testing. Environ. Res. 12, pp. 358-365, 1976.

10. Bertsch, W. and E. Anderson. Characterization of Coal-Derived Fluids by Capillary Column GC-MS, J. Chromatograph. 126, pp. 213-224, 1976.

11. Wiser, W.H.. Paper presented at Short Course on Coal Conversion Processes, OCT. -Nov. 1973, Pennsylvania State University.

12. Guerin, M.R., W.H. Giest, C.H. Ho, W.D. Schultz, Proc. 3rd Environmental Protection Conference, Chicago, Ill. Sept. 23-26 1975, pp. 661-85.

APPENDIX A

Protocol of GC-MS Identification Procedure

To identify the many compounds contained in each fraction produced by the resin chromatographic separation, a GC-MS equipped with a computer library of mass spectra of 31,331 compounds was used. The peaks eluting from the GC can be individually and immediately analyzed for their mass spectra which can then be compared to those in the computer library. The three best matching spectra are then printed for visual inspection.

A quantitative assessment of the match between the sample peak spectrum and a given library spectrum is provided in the "fit," "reverse fit," and "purity" indices. These are based on scales of 1 to 1000. "Fit" describes how well the library spectrum fits into the sample spectrum. "Reverse fit" describes how well the sample spectrum fits into the library spectrum. "Purity" is the Boolean algebra dot product of the two. While fits should be in the 800's and 900's for confidence in identification, a lower purity index need not discount the match. Purities can vary rarely be above 900, so values between 500 and 900 merit confidence if their fits are good. In some cases, the discretion of the mass spectroscopist is called into play to choose among closely ranking matches.

Not all the data and spectra match candidates will be presented here. Survey analysis summaries of the best matches for each peak with their purity, fit, and reverse fit indices, are presented in Table 47 through 58. The complete data are on file in this laboratory , and are open to perusal at any request.

By way of explanation, all the data for water sample No. 1 HO neutral fraction are displayed here. The reconstructed ion chromatogram illustrates the ion amplitude associated with each peak, which are placed in the order at which elution occurred. This is shown in Figures 13 and 14. The mass spectrum of each peak is then shown with the spectra of the three best match candidates. Alongside the spectra is the library search information summary for that peak. These are shown in Tables 29-46. The composite survey analysis summary for this fraction is found in Table 47.

The composite survey analyses for other fractions of water sample No. 1 are listed in Tables 48-52. The same analysis for all six fractions of water sample No. 2 are listed in Tables 53-58.

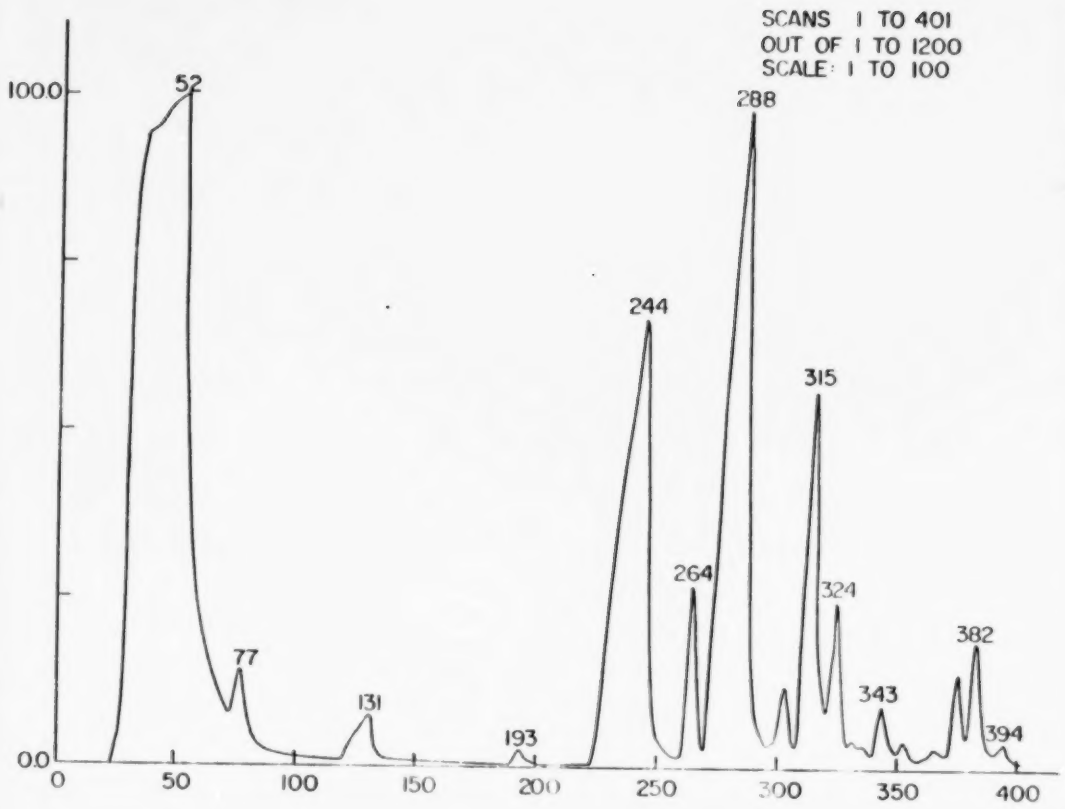


FIGURE 13. Reconstructed Ion Chromatogram [illegible] Water Sample No. [illegible]
Hydrophobic Neutral Fraction

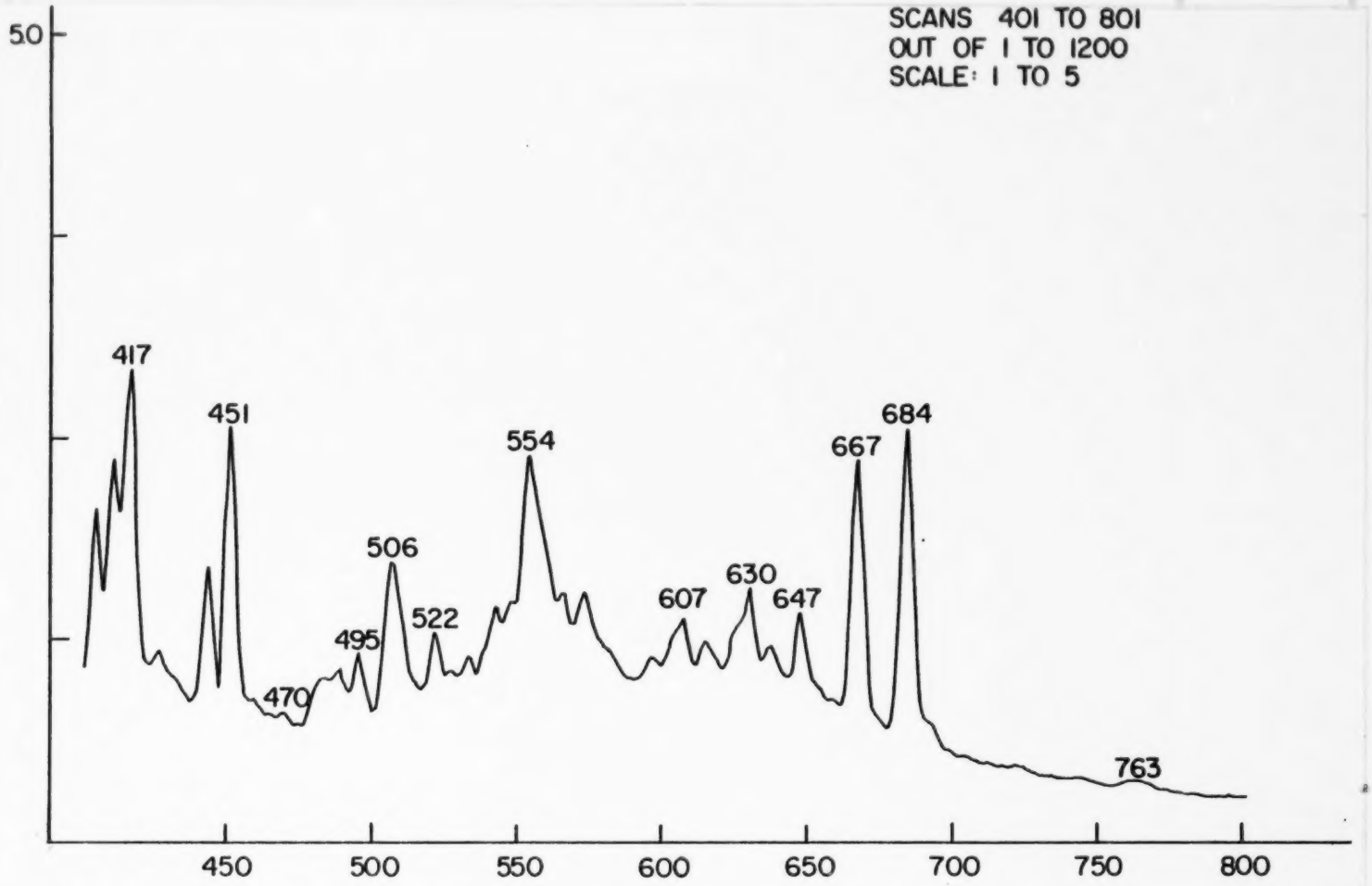
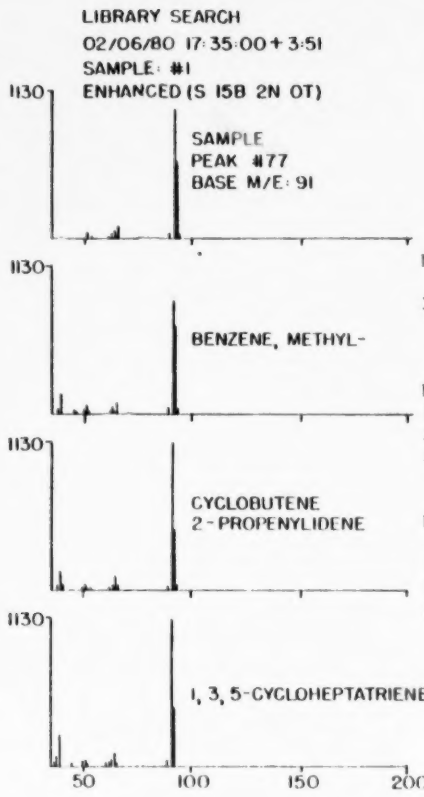


FIGURE 14. Reconstructed Ion Chromatogram Water Sample No. 1
Hydrophobic Neutral Fraction



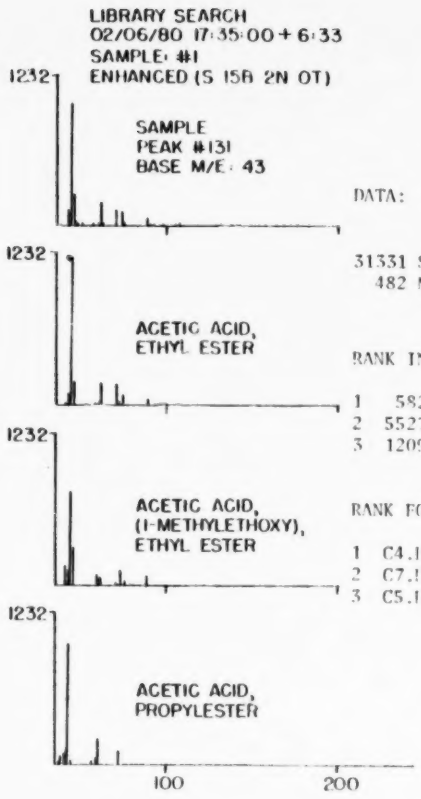
DATA: 1110201 #77 BASE M/E: 91

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
445 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	690	BENZENE, METHYL-
2	697	CYCLOBUTENE, 2-PROPENYLIDENE
3	692	1,3,5-CYCLOHEPTATRIENE

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C7.H8	92	91	965	981	977
2	C7.H8	92	91	955	977	963
3	C7.H8	92	91	941	979	952

TABLE 29. PEAK #77, M/E 91



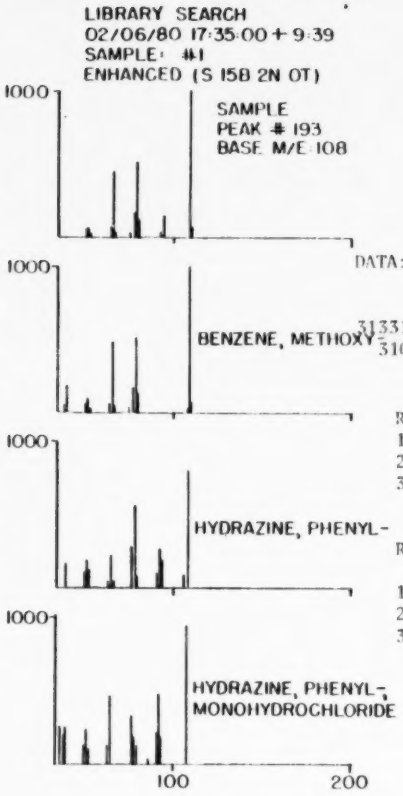
DATA: 1110201 #131 BASE M/E: 43

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
482 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	582	ACETIC ACID ETHYLESTER
2	5527	ACETIC ACID, (1-METHYLETHOXY) -, ETHYL ESTER
3	1209	ACETIC ACID, PROPYLESTER

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C4.H8.O2	88	43	903	951	916
2	C7.H14.O3	146	43	747	777	837
3	C5.H10.O2	102	43	695	839	746

TABLE 30. PEAK 131, M/E 43



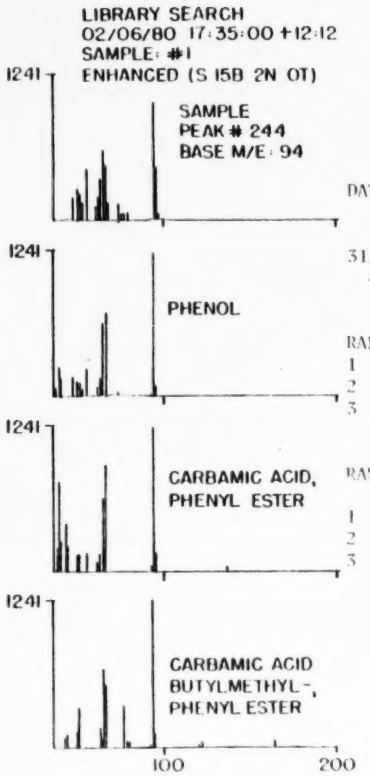
DATA: 1110201 #193 BASE M/E: 108

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
310 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	1505	BENZENE, METHOXY-
2	1482	HYDRAZINE, PHENYL-
3	5159	HYDRAZINE, PHENYL-MONOHYDROCHLORIDE

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C7.H8.O	108	108	897	977	917
2	C6.H8.N2	108	108	786	838	827
3	C6.H9.N2.CL	144	108	729	783	749

TABLE 31. PEAK #193, M/E 108



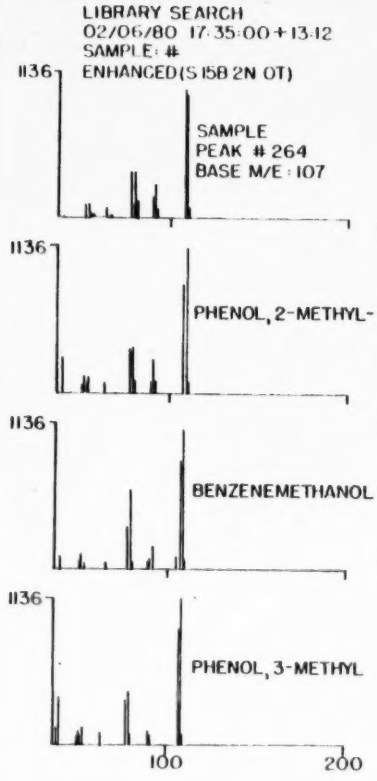
DATA: 1110201 #244 BASE M/E: 94

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
412 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	730	PHENOL
2	4263	CARBAMIC ACID, PHENYLESTER
3	13710	CARBAMIC ACID, BUTYLMETHYL-, PHENYL ESTER

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C6.H6.O	94	94	769	902	775
2	C7.H7.O2.N	137	94	636	815	711
3	C12.H17.O2.N	207	94	614	821	656

TABLE 32. PEAK #244 M/E 94



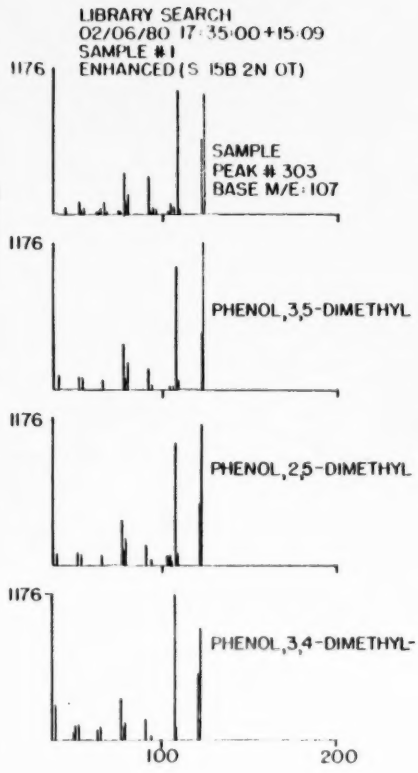
DATA: 1110201 # 264 BASE M/E: 107

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
403 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 1503 PHENOL,2-METHYL-
2 1504 BENZENEMETHANOL
3 1507 PHENOL,3-METHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C7.H8.O	108	108	949	982	960
2	C7.H8.O	108	108	915	949	915
3	C7.H8.O	108	108	902	973	915

TABLE 33. PEAK 264 M/E 107



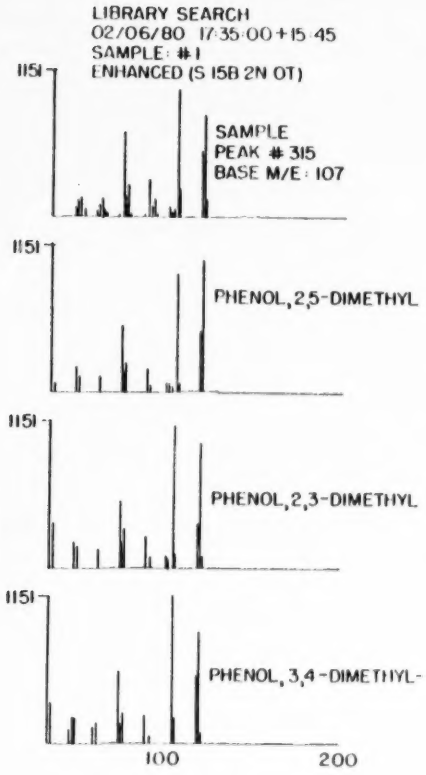
DATA: 1110201 #303 BASE M/E: 107

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
304 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	2641	PHENOL, 3,5-DIMETHYL-
2	2635	PHENOL, 2,5-DIMETHYL-
3	2634	PHENOL, 3,4-DIMETHYL-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C8.H10.O	122	122	914	980	914
2	C8.H10.O	122	122	905	971	922
3	C8.H10.O	122	107	888	981	894

TABLE 34. PEAK #303 M/E 107



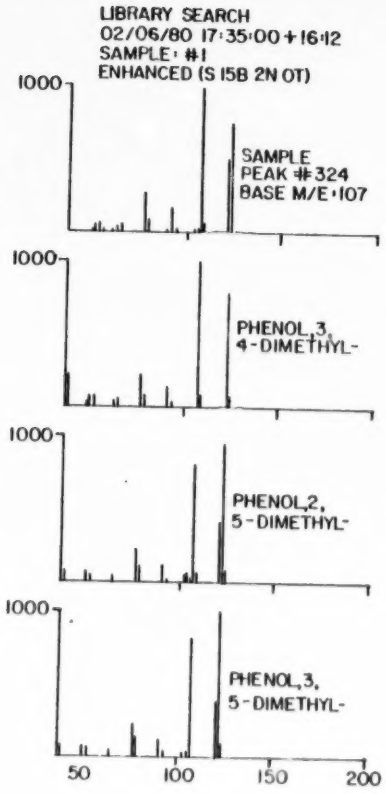
DATA: 110201 #315 BASE M/E: 107

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
305 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	2635	PHENOL, 2,5-DIMETHYL
2	2643	PHENOL, 2,3-DIMETHYL
3	2634	PHENOL, 3,4-DIMETHYL

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	REIT
1	C8.H10.O	122	122	879	978	879
2	C8.H10.O	122	107	878	978	878
3	C8.H10.O	122	107	877	983	877

TABLE 35. PEAK 315 M/E 107



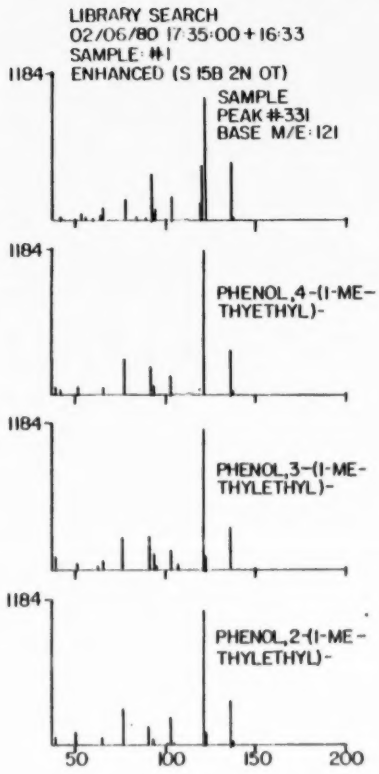
DATA: 1110201 #324 BASE M/E: 107

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
793 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK INDEX NAME
1 2634 PHENOL, 3,4-DIMETHYL-
2 2635 PHENOL, 2,5-DIMETHYL-
3 2641 PHENOL, 3,5-DIMETHYL-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C8.H10.O	122	107	933	997	933
2	C8.H10.O	122	122	929	982	929
3	C8.H10.O	122	122	926	984	926

TABLE 36. PEAK #324 M/E 107



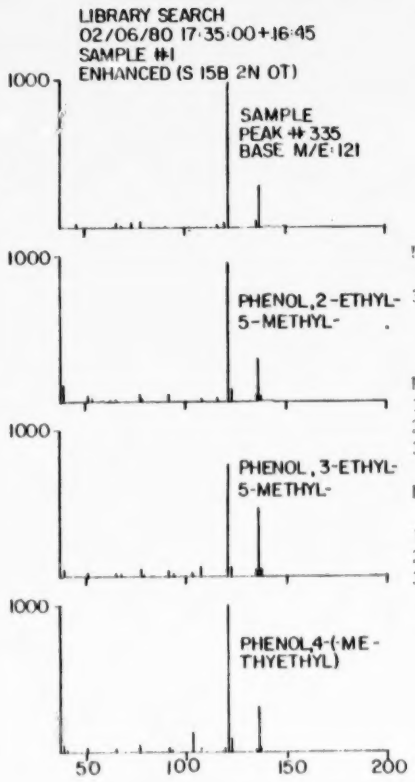
DATA: 1110201 #331 BASE M/E: 121

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
422 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	4198	PHENOL, 4-(1-METHYLETHYL)-
2	4207	PHENOL, 3-(1-METHYLETHYL)-
3	4196	PHENOL, 2-(1-METHYLETHYL)-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C9.H12.O	136	121	751	810	818
2	C9.H12.O	136	121	745	821	806
3	C9.H12.O	136	121	721	802	777

TABLE 37. PEAK #331 M/E 121



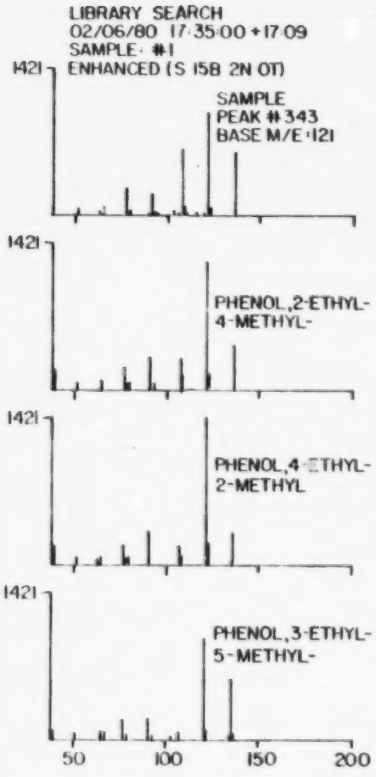
DATA: 1110201 #335 BASE M/E: 121

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
378 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	INDEX	NAME
1	4218	PHENOL,2-ETHYL-5-METHYL-
2	4214	PHENOL,3-ETHYL-5-METHYL-
3	4198	PHENOL,4-(1-METHYLETHYL)-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C9.H12.O	136	121	788	881	881
2	C9.H12.O	136	121	754	841	861
3	C9.H12.O	136	121	746	824	889

TABLE 38. PEAK #335 M/E 121



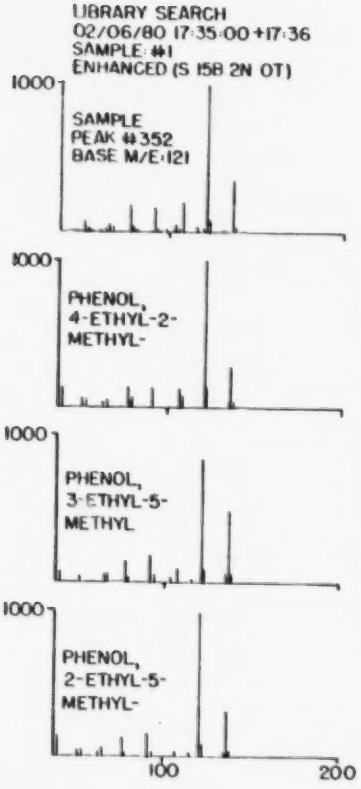
DATA: 1110201 #343 BASE M/E:121

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
724 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK INDEX NAME
1 4222 PHENOL,2-ETHYL-4-METHYL-
2 4220 PHENOL,4-ETHYL-2-METHYL-
3 4214 PHENOL,3-ETHYL-5-METHYL-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C9.H12.0	136	121	828	922	861
2	C9.H12.0	136	121	798	891	810
3	C9.H12.0	136	121	760	886	780

TABLE 30. PEAK #343 M/E 121



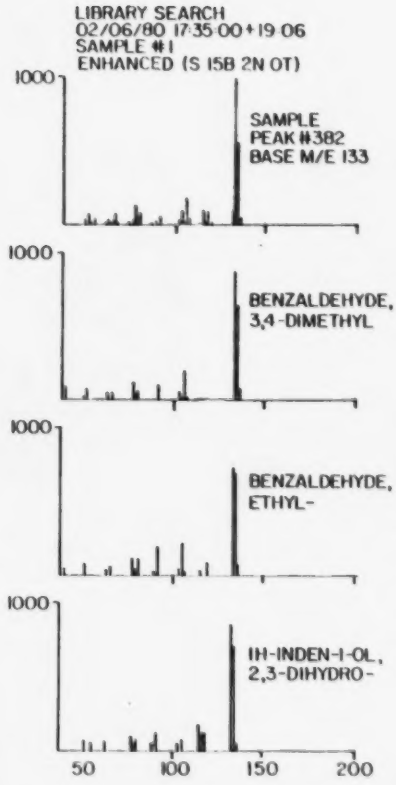
DATA: 1110201 #352 BASE M/E:121

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
743 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 4220 PHENOL,4-ETHYL-2-METHYL-
2 4214 PHENOL,3-ETHYL-5-METHYL-
3 4218 PHENOL,2-ETHYL-5-METHYL-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C9.H12.O	136	121	869	961	885
2	C9.H12.O	136	121	856	939	879
3	C9.H12.O	136	121	846	941	860

TABLE 40. PEAK #352 M/E 121



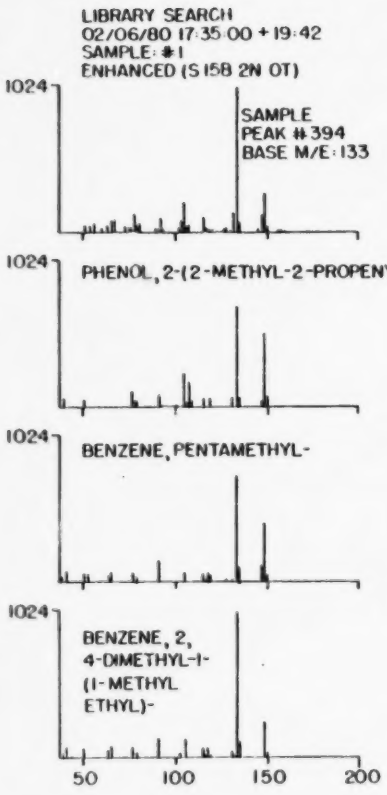
DATA: 1110201 #382 BASE M/E: 133

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
734 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 3967 BENZALDEHYDE,3,4-DIMETHYL-
2 3974 BENZALDEHYDE,ETHYL-
3 3968 1H-INDEN-1-OL,2,3-DIHYDRO-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C9.H10.0	134	133	808	989	808
2	C9.H10.0	134	133	804	954	804
3	C9.H10.0	134	133	804	946	804

TABLE 41. PEAK #382 M/E 133



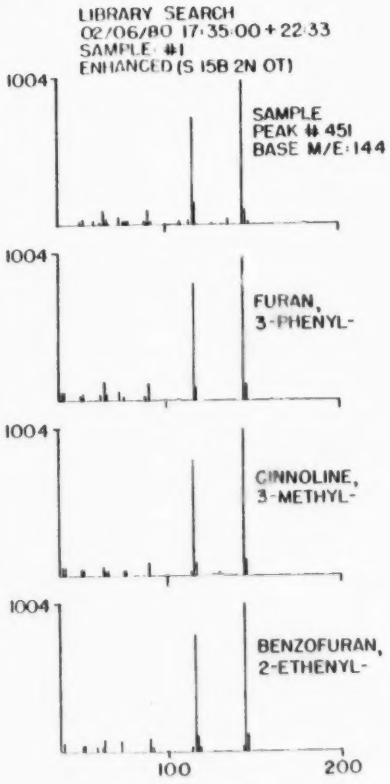
DATA: 1110201 #394 BASE M/E: 133

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
554 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 5710 PHENOL,2-(2-METHYL-2-PROPENYL)
2 5717 BENZENE,PENTAMETHYL-
3 5728 BENZENE,2,4-DIMETHYL-1-(1-METHYLETHYL)-

RANK	FORMULA	M.WT.	B.PK.	PURITY	FIT	RFIT
1	C10.H12.O	148	133	767	918	780
2	C11.H16	148	133	762	902	788
3	C11.H16	148	133	762	940	784

TABLE 42. PEAK #394 M/E 133



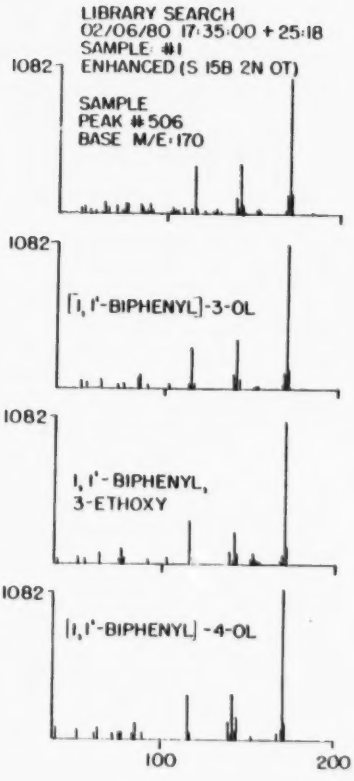
DATA: 1110201 #451 BASE M/E: 144

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
245 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 5127 FURAN,3-PHENYL-
2 5327 CINNOLINE,3-METHYL-
3 5126 BENZOFURAN,2-ETHENYL-

RANK	FORMULA	M.WT.	B.PK	PURITY	FIT	REIT
1	C10.H8.O	144	144	846	974	862
2	C9.H8.N2	144	144	819	973	837
3	C10.H8.O	144	144	815	958	842

TABLE 43. PEAK #451 M/E 144



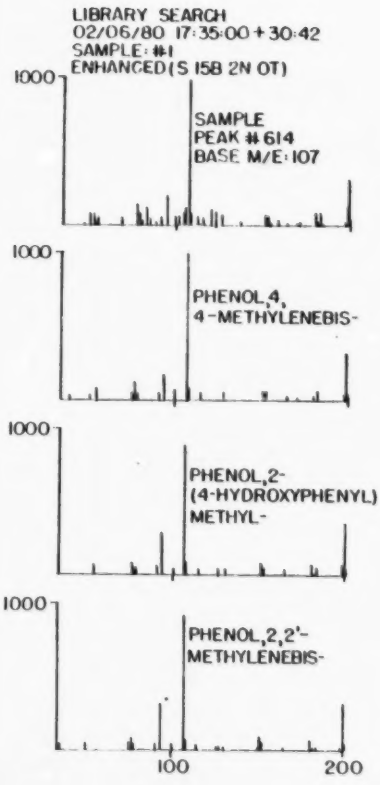
DATA: 1110201 #506 BASE M/E: 170

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
. 905 MATCHED AT LEAST 3 OF 16 LARGEST PEAKS IN THE UNKNOWN

RANK	IN	NAME
1	8968	[1,1'-BIPHENYL]-3-OL
2	12658	1,1'-BIPHENYL,3-ETHOXY-
3	8964	[1,1'-BIPHENYL]-4-OL

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C12.H10.O	170	170	786	971	801
2	C14.H14.O	198	170	741	938	759
3	C12.H10.O	170	170	732	939	749

TABLE 44. PEAK #506 M/E 170



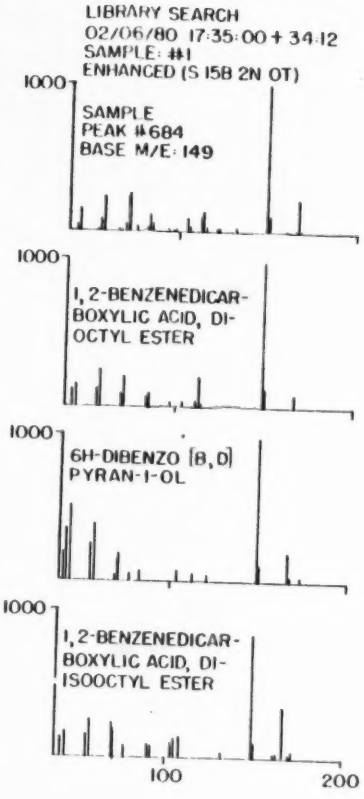
DATA: 1110201 #614 BASE M/E: 107

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
269 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 12868 PHENOL,4,4'-METHYLENEBIS-
2 12873 PHENOL,2-[(4-HYDROXYPHENYL)METHYL]-
3 12872 PHENOL,2,2-METHYLENEBIS-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C13.H12.02	200	107	657	943	688
2	C13.H12.02	200	107	637	923	678
3	C13.H12.02	200	107	598	881	645

TABLE 45. PEAK #614 M/E 107



DATA: 1110201 #684 BASE M/E: 149

31331 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
445 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 26918 1,2-BENZENEDICARBOXYLICACID,DIOCTYL ESTER
2 23962 6H-DIBENZO[B,D]PYRAN-1-OL,3-HE
3 26916 1,2-BENZENEDICARBOXYLICACID,DIISOOCTYL ESTER

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C24.H38.04	390	149	750	861	775
2	C22.H32.02	328	149	694	798	833
3	C24.H38.04	390	149	645	820	759

TABLE 46. PEAK #684 M/E 149

TABLE 47. GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC NEUTRAL FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
methylbenzene	77	965	981	977
ethyl acetate	131	903	951	916
methoxybenzene	193	897	977	917
phenol	244	769	902	775
2-methylphenol	264	949	982	960
3-methylphenol	286	938	982	947
3,5-dimethylphenol	303	914	980	914
2,5-dimethylphenol	315	879	978	879
3,4-dimethylphenol	324	933	997	933
4-(1-methylethyl)phenol	331	751	810	818
2-ethyl-5-methylphenol	335	788	881	881
2-ethyl-4-methyl-phenol	343	828	922	861
4-ethyl-2-methyl-phenol	352	869	961	885
3,4-dimethylbenzaldehyde	382	808	989	808
pentamethylbenzene	394	762	902	788
3-phenylfuran	451	846	974	862
(1.1'-biphenyl)-3-ol	506	786	971	801
4,4'-methylenebis-phenol	614	657	943	688
1,2-benzene dicarboxylic acid dioctyl ester	684	645	820	759

TABLE 48. GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC BASIC FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
phenol	69	855	932	904
2-methylphenol	86	952	984	952
3-methylphenol	91	929	918	936
4-methylphenol	99	862	940	893
aniline hydrochloride	76	743	848	828

TABLE 49. GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC ACIDIC FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
cyclohexenone	52	530	782	637
anisole	59	884	985	892
phenol	74	800	900	900
2-methylphenol	98	943	989	943
aniline	84	836	980	881
dimethylphenol isomer	135	764	927	787

TABLE 50. GC-MS COMPUTER MATCH SUMMARY
HYDROPHILIC NEUTRAL FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
xylene	49	653	962	875
1-chloro-2,4,-dimethyl benzene	93	884	997	884
2-methly-2-cyclopenten-1-one	124	545	879	606
4,7 dimethyl undecane	207	860	952	869

TABLE 51.GC-MS COMPUTER MATCH SUMMARY
HYDROPHILIC BASIC FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
anisole	59	885	989	894
phenol	77	901	959	935
chloroxylene isomer	91	831	972	854
2-methylphenol or isomer	99	942	996	942
3-methylphenol or isomer	105	927	994	928
1-bromo-2-methoxy-benzene	146	774	961	792

TABLE 52. GC-MS COMPUTER MATCH SUMMARY
HYDROPHILIC ACIDIC FRACTION OF WATER SAMPLE NO. 1

Compound	Peak No.	Purity	Fit	Reverse Fit
methyl hexanoic acid	54	843	939	891
xylene	47	851	931	886
anisole	60	901	999	901
phenol	77	867	957	892
chloroxylene isomer	91	865	999	965
3-methylphenol	105	556	977	564
methyl benzoate	116	827	962	858
1-bromo-2-methoxy-benzene	145	793	962	806
dimethyl pimelic acid	163	629	901	685
methyl ester of benzenepropanoic acid	169	753	928	805
dimetnyl phthalate	234	644	915	687

TABLE 53 . GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC NEUTRAL FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
benzene, methoxy	167	865	961	896
phenol	224	852	964	859
2-methyl phenol	254	934	974	945
2,5-dimethyl phenol	280	816	858	893
2-ethyl phenol	290	902	951	936
2,3,-dimethyl phenol	295	923	987	923
2,3,-dimethyl phenol	306	918	984	918
3,4,-dimethyl phenol	318	924	996	924
4-(1-methylethyl-phenol)	326	841	912	915
2-ethyl-5-methyl phenol	331	874	960	909
2-(1,1-dimethylethyl)- phenol	357	753	885	836
3,4,-dimethyl benzaldehyde	379	841	992	841
4-ethyl -1,3, -benzenediol	429	771	912	818
(1,1-biphenyl) -2,2'-diol	606	715	820	847
1,2,-benzenedicarboxylic acid, dioctyl ester	680	521	751	648
3-methyl phenol	262	949	991	949

TABLE 54 . GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC BASIC FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
methyl pyridine	37	855	974	870
dimethyl pyridine (isomers)	48	845	943	876
ethyl pyridine	**54**	**577**	**642**	**690**
Phenylhydrazine	58	877	998	877
dimethyl pyridine isomer	65	805	897	848
phenol	79	780	935	809
4-methyl pyridine	**86**	**763**	**912**	**803**
methyl ethyl pyridine	141	842	986	842
quinoline	171	942	998	942
1,2,3,4 tetrahydroquinoline	196	816	967	816
2-methyl quinoline	187	870	998	870

TABLE 55. GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC ACIDIC FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
methoxybenzene	56	905	990	914
phenol	75	894	953	936
chloroxylene or -chloroxylene	88	680	933	726
	88	678	930	718
1-bromo-2-methoxy-benzene	145	787	899	839

TABLE 56 GC-MS COMPUTER MATCH SUMMARY
HYDROPHOBIC ACIDIC FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
2-pentenal-2 methyl or isomer	36	888	962	865
anisole	57	917	999	917
xylene isomer	43	816	860	944
chloroxylene isomer	89	730	979	743
chloroxylene isomer	115	514	890	548

TABLE 57. GC-MC COMPUTER MATCH SUMMARY
HYDROPHOBIC ACIDIC FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
2-methyl-2 pentenal	38	848	964	877
anisole	58	901	989	910
phenol	76	909	970	935
chloroxylene isomer	89	848	978	864
2-methyl phenol	97	903	992	903
3-methyl phenol	104	921	992	921
3-ethyl phenol	133	739	994	739

TABLE 58 . GC-MC COMPUTER MATCH SUMMARY
HYDROPHOBIC ACIDIC FRACTION OF WATER SAMPLE NO. 2

Compound	Peak No.	Purity	Fit	Reverse Fit
xylene	45	872	928	912
anisole	58	887	990	895
phenol	78	589	871	675
chloroxylene	90	854	971	876
chloromethyl toluene	116	606	975	615
dichloroxylene	142	646	897	708
1-bromo-2-methoxy-benzene	145	824	979	830

Appendix B

EPA Priority Pollutant List

NO.	COMPOUND	NO.	COMPOUND
1	acenaphthene	28	3,3'-dichlorobenzidine
2	acrolein	29	1,1-dichloroethylene
3	acrylonitrile	30	1,2-trans-dichloroethylene
4	benzene	31	2,4-dichlorophenol
5	benzidine	32	1,2-dichloropropane
6	carbon tetrachloride	33	1,3-dichloropropylene
7	chlorobenzene	34	2,4-dimethylphenol
8	1,2,4-trichlorobenzene	35	2,4-dinitrotoluene
9	hexachlorobenzene	36	2,6-dinitrotoluene
10	1,2-dichloroethane	37	1,2-diphenylhydrazine
11	1,1,1-trichloroethane	38	ethylbenzene
12	hexachloroethane	39	fluoranthene
13	1,1-dichloroethane	40	4-chlorophenyl phenyl ether
14	1,1,2-trichloroethane	41	4-bromophenyl
15	1,1,2,2-tetrachloroethane	42	bis(2-chloroisopropyl)ehter
16	chloroethane	43	bis(2-chloroethoxy)methane
17	bis(chloromethyl)ether	44	methylene chloride
18	bis(2-chloroethyl)ether	45	methyl chloride
19	2-chloroethylvinyl ether	46	methyl bromide
20	2-chloronaphthalene	47	bromoform
21	2,4,6-trichlorophenol	48	dichlorobromomethane
22	parachlorometa cresol	49	trichlorofluoromethane
23	chloroform	50	dichlorodifluoromethane
24	2-chlorophenol	51	chlorodibromomethane
25	1,2-dichlorobenzene	52	hexachlorobutadiene
26	1,3-dichlorobenzene	53	hexachlorocyclopentadiene
27	1,4-dichlorobenzene	54	isophorone

NO.	COMPOUND	NO.	COMPOUND
55	naphthalene	86	toluene
56	nitrobenzene	87	trichloroethylene
57	2-nitrophenol	88	vinyl chloride
58	4-nitrophenol	89	aldrin
59	2,4-dinitrophenol	90	dieldrin
60	4,6-dinitro-o-cresol	91	chlordane
61	N-nitrosodimethylamine	92	4,4'-DDT
62	N-nitrosodiphenylamine	93	4,4'-DDE
63	N-nitrosodi-n-propylamine	94	4,4'-DDD
64	pentachlorophenol	95	α-endosulfan
65	phenol	96	ß-endosulfan
66	bis(2-ethylhexyl)phthalate	97	endosulfan sulfate
67	butyl benzyl phthalate	98	endrin
68	di-n-butyl phthalate	99	endrin aldehyde
69	di-n-octyl phthalate	100	heptachlor
70	diethyl phthalate	101	heptachlor epoxide
71	dimethyl phthalate	102	α-BHC
72	benzo(a)anthracene	103	ß-BHC
73	benzo(a)pyrene	104	γ-BHC
74	3,4-benzofluoroanthene	105	δ-BHC
75	benzo(k)fluoranthene	106	PCB-1242
76	chrysene	107	PCB-1254
77	acenaphthylene	108	PCB-1221
78	anthracene	109	PCB-1232
79	benzo(ghi)perylene	110	PCB-1248
80	fluorene	111	PCB-1260
81	phenanthrene	112	PCB-1016
82	dibenzo(a,h)anthracene	113	toxaphene
83	ideno(1,2,3-cd)pyrene	129	2,3,7,8-tetrachlorodibenzo-p-dioxin
84	pyrene		
85	tetrachloroethylene		